BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

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General, Physical, and Inorganic Chemistry.

Absorption spectrum of thallium vapour between 7000 and 1850 Å. R. G. Loyarte and A. T. Williams (J. Phys. Radium, 1928, [vi], 9, 121—126).—Observations on the absorption spectrum of thallium vapour between 700° and 900° show, in agreement with Grotrian (A., 1923, ii, 106) and others, the lowest level to be $^2P_1$ and all the corresponding lines of the series $^2P_1-{}^2S_1$ and $^2P_1-{}^2D_2$ have been observed. At 700° and below, some lines corresponding with the level $^2P_2$ appear, but they are fewer than in the case of aluminium, gallium, or indium. No trace of the green line 5350·46 Å. could be detected. Sharp, fine lines between 2210 and 2105 Å., previously recorded as band or diffuse lines by earlier workers, have been observed. L. S. Theobald.

Filtration of arc and spark lines in a magnetic field by using disruptive discharge in a vacuum. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1928, 4, 195—197).—The method of separating arc and spark lines in a spectrum by using the disruptive discharge in a strong magnetic field (cf. this vol., 339) gives ambiguous lines in some cases, due to the resistance of the air to the motion of the ions. This can be prevented by using the discharge in a vacuum. An apparatus is described by means of which this can be studied. A. J. Mee.

Influence of energy factors on the structure of spectra. T. Negresco (J. Chim. phys., 1928, 25, 308—319).—The influence of temperature on flame spectra and of the nature of the electrodes, the surrounding atmosphere, the potential gradient between the electrodes, and the nature of the current on arc and spark spectra is discussed, and also the effect of self-induction on the spark discharge and its spectrum. The emission of radiation of low potential is not due solely to the hot envelope of metallic vapour, but is primarily an electrical effect. The effect of self-induction is due to the lowering of the potential gradient in the initial discharge, which causes an increase in the intensity of the radiations due to the subsequent oscillations. W. A. Richardson.

Series in the spark spectra of germanium. K. R. Rao and A. L. Narayan (Proc. Roy. Soc., 1928, A, 119, 607—627).—The spark spectrum of germanium has been investigated over the range 6484·32—2099·98 Å. A small quantity of germanium was fused to the tips of pure tin rods, which were used as electrodes between which the spark took place. The spark was studied in an atmosphere of hydrogen under varying conditions, the spectra being photographed by a 5-foot concave grating and a large Hilger quartz spectrograph. The region below 2400 Å. was photographed on Schumann plates. Detailed descriptions and analyses are given of the spectra of singly-ionised (Ge II), doubly-ionised (Ge III), and trebly-ionised (Ge IV) germanium, and the results are in complete agreement with the Pauli–Heisenberg–Hund theory. The second ionisation potential is computed to be about 15·88 volts, and the third about 33·17 volts. A characteristic group of lines has been observed which appears more intensely under weaker stimuli. When the excitation is a maximum the lines disappear, but the inclusion of self-induction brings them out clearly. As such, their behaviour is similar to that of arc lines, but their presence has not been recorded by any previous investigator of the arc spectrum of germanium. A table is given of all the lines of germanium which have been classified. L. L. Bircumshaw.

Intensity ratio of the doublets of the principal series of the alkali metals. H. Jacob (Ann. Physik, 1928, [iv], 86, 449—493).—The intensity ratio of the components of the second doublet of the principal series of potassium, rubidium, and cæsium has been measured by means of Merton's method. The lines were produced at the highest possible temperature (2600°) by the use of an oxy-hydrogen flame. The values of *K*, the intensity ratio, were found to vary between 1·80 and 2·02. In the case of rubidium and of cæsium the method of Gouy was used in addition for the purpose of obtaining the "true" intensity ratio. The "true" intensity ratio for the cæsium lines approximates to 4·0. For rubidium the ratio is evidently greater than 2·3, but the value of the "true" intensity ratio was not reached. W. E. Downey.

Intensity of spectral lines. A. Kupper (Ann. Physik, 1928, [iv], 86, 511—529).—Mathematical. Calculations based on Schrödinger's wave equation lead to values for the intensities of the lines of the Balmer, Paschen, Brackett, and 5th series. W. E. Downey.

Intensity ratio of the ortho- and para-series in relation to the structure of the helium atom. J. Stark (Ann. Physik, 1928, [iv], 86, 530—540).—A helium line arising from the 1*s* state cannot be detected. The ratio of the intensity of the para-series of helium to that of the corresponding ortho-series decreases with increasing gas pressure. The ratio is greater, for a given pressure, when the excitation is due to fast cathode rays than when slow cathode rays are used. The para-series correspond with the singlet series of the alkaline-earth metals,

the ortho-series to the triplet ones. The spectral and structural similarity of helium and the alkaline-earth metals leads to the view that a para-state is less stable and, therefore, less frequent than the corresponding ortho-state.
W. E. Downey.

Spectrum of ionised sodium. F. H. Newman (Nature, 1928, **122**, 97).—The author's pairs of wave-number differences in the Na II spectrum do not appear to be accidental (cf. Laporte, this vol., 680).
A. A. Eldridge.

Spark spectrum of palladium (Pd II). A. G. Shenstone (Physical Rev., 1928, [ii], **32**, 30—38).—The analysis of the spectrum of Pd II differs from that of McLennan and Smith (A., 1926, 875). The terms include $4d\,^2D(4d^9)$; $5s\,^{4\,\&\,2}F$, $^{4\,\&\,2}P$, ^2D, $^2G(4d^85s)$; all the related triads from the structure $4d^85p$; $6s\,^{4\,\&\,2}F$, $^4P_3$, $^2G_5(4d^86s)$; and fragments of terms due to $4d^85d$. Zeeman effects for most of the lines have been measured. The ionisation potential is calculated as 19·8 volts from $4d^9$ to $4d^8$.
A. A. Eldridge.

Structure of the resonance line, 6708 Å., of the lithium arc spectrum; isotope effect with lithium. H. Schüler and K. Wurm (Naturwiss., 1927, **15**, 971—972; Chem. Zentr., 1928, i, 644).—A weak third component, situated towards the red, of the lithium resonance line 6708 Å. is recorded, and is considered to be a component of the Li^6 doublet.
A. A. Eldridge.

Polarisation of resonance radiation of cadmium. P. Soleillet (Compt. rend., 1928, **187**, 212—214).—The effect of a magnetic field on the lines 3261 and 2288 Å. in the resonance spectrum of cadmium has been investigated, the exciting radiation being unpolarised. In a zero field, or one in the same direction as the incident light, the maximum polarisation is 85% for 3261 Å. and 60% for 2288 Å. The two orbits of the $2'P_1$ level have different stabilities, and durations of about 2×10^{-6} sec. and 10^{-9} sec., respectively.
C. W. Gibby.

Optically excited iodine bands with alternate missing lines. R. W. Wood and F. W. Loomis (Phil. Mag., 1928, [vii], **6**, 231—238).—The fluorescence spectrum of iodine enhanced by the presence of helium at 0·5 mm. pressure has been examined and the fluorescence lines have been found to correspond exactly with the absorption lines with even initial rotational quantum numbers, and the alternate lines to be missing in the fluorescence bands. It then follows that, since the original excited iodine molecules after absorbing light and immediately before colliding with helium atoms had the rotational quantum number 34, during collisions in which the electronic quantum number is unchanged the rotational quantum number of an iodine molecule can change only by an even number. This conclusion is not in accordance with the selection principle, but is in agreement with the theory of Hund (A., 1927, 809) that the rotational states of symmetrical molecules are divided into two classes, characterised by eigen-functions symmetrical and unsymmetrical, respectively, in the position co-ordinates of the nuclei, between which transitions do not occur.
A. E. Mitchell.

Afterglow in mixtures of nitrogen and oxygen. B. Lewis (Nature, 1928, **122**, 241).—Using an electrodeless discharge with a spark gap, at 1·8—0·01 mm., there is for a given mixture, *e.g.*, air, a sharp minimal afterglow at 0·53 mm. separating the yellowish-green oxygen afterglow (at higher pressures) from the orange-yellow nitrogen afterglow (at lower pressures). In a certain pressure region near this minimum a long discharge gives a blue afterglow; the nitrogen bands also appear at a suitable pressure. With a very short discharge only the yellowish-green afterglow is visible. Thus, different types of afterglows may be excited in the same gas mixture at the same pressure merely by altering the period of discharging.
A. A. Eldridge.

Spectrum of trebly-ionised antimony, Sb IV. J. B. Green and R. J. Lang (Nature, 1928, **122**, 242).—A $^3P^3S$ multiplet between 805 and 861 Å., a very strong $^3P^3D$ multiplet between 873 and 940 Å., a $^3D^3F$ multiplet between 2077 and 2113 Å., and a possible $^3P^3P'$ group between 1051 and 1193 Å. have been identified. The ionisation potential is computed as 42 volts.
A. A. Eldridge.

Analysis of the first spark spectrum of sulphur (S^+). D. K. Bhattacharyya (Nature, 1928, **122**, 241—242).

Influence of magnetic fields on the bands of the third positive group in nitrogen. B. Pogány and R. Schmid (Z. Physik, 1928, **49**, 162—166).—Data are given for the broadening of the lines of the (0,1) and (0,2) bands of the third positive group of nitrogen in a field of 26 kilogauss.
R.. W. Lunt.

Classification of the band spectra associated with the neutral oxygen molecule. W. Ossenbrügen (Z. Physik, 1928, **49**, 617—216).—The classification of the oscillation and rotational terms in the Schumann bands of the neutral oxygen molecule is discussed in detail; by adopting the value $6{\cdot}54\times10^{-27}$ for h, the following values are derived for the moment of inertia in a motionless unexcited state and for the effective atomic radius respectively, $19{\cdot}20\times10^{-40}$ g. cm.^{2}, $0{\cdot}6005\times10^{-8}$ cm.
R. W. Lunt.

Variation of the intensity of the lines of the mercury spectrum excited by different types of discharge. T. Hori (Z. Physik, **49**, 259—268).—Qualitative data are given for the intensity of mercury lines excited by arc discharges with and without the presence of hydrogen, by low-velocity electrons from an oxide-coated cathode, and by a Geissler tube discharge. These results, which are preliminary to a quantitative investigation, indicate that the observed variations cannot be traced solely to variations in absorption; it is thought that the emission of HgH bands in the presence of hydrogen indicates that the reaction $Hg^*+H_2=HgH+H$ takes place.
R. W. Lunt.

Relative intensities of the H_α and D_3(He) lines in protuberances of the sun's chromosphere. E. J. Perepelkin (Z. Physik, 1928, **49**, 295—305).—Astronomical.
R. W. Lunt.

Intensity distribution in the negative nitrogen band spectrum. L. S. Ornstein and W. R. van Wijk (Z. Physik, 1928, **49**, 315—322).—Measurements have been made of the intensity distribution in the bands 3914, 4278, 3884, and 4237 Å. The intensity

distribution can be represented by a Boltzmann function of the rotational quantum number p of the form $\exp[-h^2p(p+1)/8\pi^2IkT]$, where h is the Planck constant, I the moment of inertia, k the Boltzmann constant, and T the absolute temperature.
R. W. Lunt.

Bands of the third positive group in nitrogen. R. Schmid (Z. Physik, 1928, 49, 428—462).—The classification of the bands (0,2), (0,3), (0,4), (1,4) by Guillery has been extended to include the bands (0,0), (0,1), (1,0), (1,1), (2,3), and (3,4).
R. W. Lunt.

Energy distribution in band spectra, especially in nitrogen bands. G. Herzberg (Z. Physik, 1928, 49, 761—773).—It is pointed out that the parabolic energy distribution in a band spectrum required by Condon's theory (A., 1927, 89) is attained only when the distribution of the molecules over the various vibration states in the initial condition is uniform. Generally this is not the case. From the theory developed by Franck (A., 1926, 583) considerable deviations would be expected, although at great activations approximations to the Condon distribution law can be attained. This has been shown experimentally with the nitrogen bands. This fact is explained by supposing that in the case of collisions between high-velocity electrons, Franck's rule is broken and vibrations of higher quantum number can be stimulated to a greater extent. J. W. Smith.

Spectroscopic data relating to the afterglow in nitrogen. G. Herzberg (Z. Physik, 1928, 49, 512—533).—The spectrum of the afterglow in nitrogen excited by the electrodeless discharge under unspecified electrical conditions has been examined with reference to the shift of the maxima of intensity in the green, yellow, and red group of bands produced by quenching the afterglow with liquid air and by alteration of the pressure. The data obtained are reviewed at length and are thought to support the hypothesis that the afterglow is due to collisions between metastable atoms despite the difficulty of interpreting Bonhoeffer's data (cf. A., 1927, 801) on this view. R. W. Lunt.

Inverse Stark effect in the principal series of sodium. W. Grotrian (Z. Physik, 1928, 49, 541—545).—The inverse Stark effect in absorption in sodium vapour at 280—320° has been measured for the doublets of the 2nd and 3rd terms of the principal in fields up to 10^2 kv. cm.$^{-1}$ In the case of the doublets 3302·94 and 3320·34 Å. the displacements are equal and linearly related with the square of the field strength; a similar relationship holds for the doublets 2852·851 and 2853·038 except that the former has a slightly greater displacement coefficient than the latter. R. W. Lunt.

Statistical derivation of the Rydberg correction for *s*-terms. E. Fermi (Z. Physik, 1928, 49, 550—554).

Ionisation of mercury atoms by reaction with helium ions. J. Stark (Ann. Physik, 1928, [iv], 86, 541—546).—The emission of mercury spark lines is much stronger in comparison with the emission of mercury arc lines for a mixture of mercury vapour and helium in the negative glow of a discharge tube than for a mixture of mercury vapour and neon. The same intense emission of the spark lines should apply in the case of the alkaline-earth and alkali metals.
W. E. Downey.

Distribution in direction of photo-electrons from alkali metal surfaces. H. E. Ives, A. R. Olpin, and A. L. Johnsrud (Physical Rev., 1928, [ii], 32, 57—80).—A study of the distribution in direction of photo-electrons emitted from surfaces of liquid alloys of sodium and potassium, and thin films of potassium or rubidium on platinum, irradiated by light incident at various angles and polarised in different planes. Some form of surface anisotropy appears to exist. A. A. Eldridge.

Complete photo-electric emission from potassium. (Miss) J. Butterworth (Phil. Mag., 1928, [vii], 6, 1—16).—Examination of the photo-electric emission from potassium has produced no evidence for the existence of a positive emission. If such does occur it is less than 10^{-7} times the negative emission or at least a thousand times smaller than the apparent positive emission reported by Dember (Ann. Physik, 1910, 30, 142). The photo-electric threshold of potassium has two work-functions corresponding with the wave-lengths 9700 and 60,000 Å., the results indicating that the "patches" (Richardson and Young, A., 1925, ii, 343) of lower work-function form a very small part of the total surface and under prolonged illumination are able to acquire the greater work-function. A. E. Mitchell.

The normal photo-electric effect. P. Lukirsky and S. Priležaev (Z. Physik, 1928, 49, 236—258).—The photo-electric effect in aluminium, zinc, tin, nickel, silver, cadmium, lead, copper, and platinum has been investigated by measuring the currents flowing from a small sphere of the metal under investigation, when illuminated by monochromatic light in the range 2302—3130 Å., to a surrounding metal sphere, as a function of the *P.D.* between the two spheres. Under such conditions the maximum electron energy $\frac{1}{2}mv^2_{\text{max.}}$ is related to the potential V_2 producing saturation current by the equation $\frac{1}{2}mv^2_{\text{max.}}=e(V_2+K)=h\nu-p_1-p_2$, where K is the contact *P.D.* between the spheres, p_1 the work of removing an electron from an atom, and p_2 the work associated with the motion of the released electron to the metal surface. The data obtained lead to the following values respectively for the critical excitation wave-lengths: 4132, 4009, 3411, 3364, 3364, 3302, 3110, 3033, and 3018 Å.; and the mean value obtained for Planck's constant is $6{\cdot}543\times10^{-27}$ erg×sec., in good agreement with the accepted value from optical data, $6{\cdot}545\times10^{-27}$. It is also shown that the contact *P.D.* between aluminium and the other metals examined is equal to the difference between the minimum quanta necessary for the excitation of photo-electrons. From this it is concluded that the electrons emitted under the influence of light are identical with those associated with electrical conduction. The velocity distribution of photo-electrons where corrected to the same maximum velocity and photo-electric current varies somewhat in the metals examined, which is thought to be due to the different light penetration and corresponding differences in the work terms, p_2. The velocities of the photo-electrons become more uniform and approximate closely to the maximum velocity as the thickness of the irradiated metal layer is reduced.

R. W. Lunt.

Photo-electric effect with sub-microscopic drops. K. Scharf (Z. Physik, 1928, **49**, 827—857).—The photo-electric properties of mercury, bismuth, selenium, and sulphur particles, produced by vaporisation of the element in an atmosphere of pure nitrogen, have been investigated by Ehrenhaft's condenser method. These substances show a predominant normal photo-electric effect. Inverse charging appears only rarely in single particles, but to a much greater extent in the clouds of very small particles produced by strong heating of the substance. The number of negatively-charged particles in a cloud was found to be inversely proportional to the normal sensitivity of the element, which decreases with the different elements in the order given above.

J. W. Smith.

Nature of gaseous ions. L. B. Loeb (Physical Rev., 1928, [ii], **32**, 81—96).—For pure gases the dielectric attraction of the molecules by the charged ion can account for the order of magnitude of the mobility on either the cluster or the small ion theory. Blanc's law is not universally valid. Mobility curves in mixtures indicate three types of effect: absence of clustering, labile clustering, and stable clustering. Clusters approaching in their stability and nature definite chemical combinations are postulated. A. A. Eldridge.

Energy of radiation excited by electronic bombardment. P. Bricout (J. Phys. Radium, 1928, [vi], **9**, 88—119).—An apparatus is described for the determination of the relation between the energy of the electrons emitted from a hot filament and the intensity of the radiation excited by them, and a method of measuring the absolute value of the energy emitted is developed. A theoretical explanation of the results is discussed, and a calculation made of the probability of the emission of a quantum of energy due to a collision between an electron and a neutral atom. W. A. Richardson.

New method of determining the mobility of ions or electrons in gases. R. J. van de Graaff (Phil. Mag., 1928, [vii], **6**, 210—217).—The results of most measurements of the velocity of ions or electrons in the direction of an electric force represent the upper or lower limits of the mean velocities due to variable conditions. A method for measuring the mean velocity of a group of ions moving in a gas under a steady electric force is described. The method involves the superposition, on a plate and grid combination in the gas under examination, of the shuttering effect of an oscillating potential of known frequency which allows the transference of ions during definite time intervals. Measurements of the distances and the maximum currents in the gas then provide all the necessary data. The mobility of the positive ions of hydrogen at 760 mm. has been found to be 5·8 cm./sec., which is approximately the mean of values given by other workers. A. E. Mitchell.

Reflexion of electrons. S. Szczeniewski (Compt. rend., 1928, **187**, 106—109).—The reflexion of cathode rays from the cleavage surface of a bismuth crystal has been measured for different angles of incidence and accelerating potentials of 62, 139, and 240 volts. The results are in agreement with the theoretical formula $\lambda=12{\cdot}22/\sqrt{v}$, where λ is the wave-length (in Å.) associated with the beam of cathode rays, and v is the fall of potential in volts. C. W. Gibby.

Constitution of germanium. F. W. Aston (Nature, 1928, **122**, 167).—Experiments with germanium tetraethyl and tetrafluoride indicate that germanium has the following isotopes, in order of descending intensity: 74, 72, 70, 73, 75, 76, 71, 77. It is unlikely that any of these lines is due to hydrogen compounds, but the intensity of Ge^{76} is in doubt. Of these mass numbers only 72 and 73 are peculiar to germanium. A. A. Eldridge.

At. wt. of proto-actinium. F. Lotze (Naturwiss., 1928, **16**, 558).—Since 6 α-particles are lost in the degeneration of proto-actinium to actinium-*D*, and since at. wt. determinations on lead of radioactive origin lead to the mean value of 207·42 for the at. wt. of actinium-*D*, it is suggested that the most probable value for the at. wt. of protoactinium is 231.

R. W. Lunt.

Dependence of the photographic action of β-rays on their velocity. C. D. Ellis and G. H. Aston (Proc. Roy. Soc., 1928, **A**, **119**, 645—650).—In recent work by Ellis and Wooster (A., 1927, 393) on the relative intensities of the β-ray groups of radium-*B* and -*C*, it was assumed that photographic action ran parallel with the total ionisation per cm., *i.e.*, varied as $1/\beta^2$. This assumption has now been tested by comparing the distribution of intensity measured photographically with Gurney's data for the variation of the number of electrons with the velocity (A., 1926, 5), and it is found that photographic action varies on the whole more rapidly than $1/\beta^2$ in the region 200,000 volts and upwards. Ilford *X*-ray emulsion plates were used, and the results are expressed by a curve showing how to reduce photographic densities due to electrons of different speeds to a common basis of true exposure.

L. L. Bircumshaw.

Method of determining the volume of 1 curie of radon. L. Wertenstein (Phil. Mag., 1928, [vii], **6**, 17—33).—Pressure measurements on samples of radon of known radioactive power have been made by means of a Knudsen gauge, whilst the corresponding purity has been determined simultaneously by means of a quartz fibre gauge, the main impurity having been shown previously (this vol., 684) to be carbon dioxide. The volume of 1 curie of radon at N.T.P. is thus shown to be $6{\cdot}39\times10^{-4}\pm5\%$ c.c. Measurements in capillary tubes gave confirmatory results which were, however, rendered variable by the effect of rarefied radon in promoting gas evolution from the glass, whilst concentrated radon acts as a "clean-up" agent. The first effect is attributed to α-particle bombardment of the glass, whilst the second is explained by the bombardment of the gas molecules by α-particles and their subsequent adsorption. The considerably larger volumes obtained by Rutherford

and others are attributed to lack of sufficient information as to the purity of their material.
A. E. Mitchell.

Effects produced by positive-ion bombardment of solids : metallic ions. M. L. Oliphant (Proc. Camb. Phil. Soc., 1928, **24**, 451—469).—Experiments have been made to determine the relation between the energy of a positive ion and the effect produced on a surface which it bombards. Considerable secondary emission occurs due to layers of adsorbed gas over the target. The deposition of metal from the positive ions causes changes of the surface bombarded which are difficult to allow for.
W. E. Downey.

Recoil velocities in β-particle emission in thorium-*B*. L. Wertenstein (Z. Physik, 1928, **49**, 463).—Polemical against Donat and Philipp (this vol., 343).
R. W. Lunt.

Vaporisation of polonium in a vacuum. P. Bonèt-Maury (Compt. rend., 1928, **187**, 115—117).—A method is described for measuring the rate of vaporisation of polonium in a vacuum.
C. W. Gibby.

Kinematographic sketch of electrically exploded wires. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1928, **4**, 198—200).—Instead of photographing exploding wires on films rotating in a plane at right angles to the line of sight, as had been done previously, photographs were taken on a film moving round an axis parallel to the wire. Photographs are given of the explosion of copper and iron wires, and of magnesium ribbon. Luminous particles are expelled at right angles to the direction of flow of the current, not continuously, but in masses.
A. J. Mee.

Velocity of particles sputtered by disruptive discharge. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1928, **4**, 201—204; cf. A., 1927, 1117; this vol., 97, 339, 683).—By photographing the sputtered particles on a film rotating with known velocity and measuring the tracks, the velocity of the particles can be found. The mean velocities (in m./sec.) found are, for tungsten, 43, for magnesium, 37, and for cerium, 90, but as the speed depends on voltage, current strength, and the form of the electrodes, these values are indicative only of its order of magnitude.
A. J. Mee.

Decomposition of the lead atom. A. Smits and W. A. Frederikse (Z. Elektrochem., 1928, **34**, 350—360).—Attempts have been made to effect artificial disintegration of lead, employing quartz–mercury lamps, high-tension spark discharges and low-tension arcs through gaseous and liquid dielectrics, and irradiation. The spark and arc experiments yielded definitely negative results, but some indications of breakdown were observed by *X*-ray irradiation of lead for long periods of time. Difficultly reproducible positive results were obtained by using quartz–mercury vapour lamps, and the quartz–lead lamp remains the only method which has yielded definite results. The possibility that the result is in this case due to contamination and not to transmutation is, however, recognised.
H. F. Gillbe.

Generalisation of the Kramers–Heisenberg dispersion formula for short waves in the multi-electron problem. I. Waller (Naturwiss., 1927, **15**, 969; Chem. Zentr., 1928, i, 643).—A new dispersion formula is advanced.
A. A. Eldridge.

Contraction of hydrogen under electric discharge. R. Delaplace (Compt. rend., 1928, **187**, 225—227).—Electrolytic hydrogen, submitted to a high-tension discharge at pressures below 11 mm., undergoes an irreversible contraction, not due to the formation of H_3. Carbon monoxide and methane are found after the discharge.
C. W. Gibby.

Statistical deduction of some properties of the atom. Calculations of Rydberg's correction. E. Fermi (Atti R. Accad. Lincei, 1928, [vi], **7**, 726—730).—Mathematical.

Theory of electric conduction. W. H. McCrea (Proc. Camb. Phil. Soc., 1928, **24**, 438—444).—Mathematical (cf. Sommerfeld, this vol., 681).
W. E. Downey.

Electronic theory of metals according to wave-mechanical statistics ; Volta effect. A. Sommerfeld (Ber., 1928, **61**, [*B*], 1171—1180).—A lecture.
H. Wren.

Wave-mechanical theory of metallic conductivity. J. Frenkel and N. Mirolubow (Z. Physik, 1928, **49**, 885—893).—Mathematical (cf. Frenkel, this vol., 577).
J. W. Smith.

Undulating theory of two-electron orbits. A. W. Conway (Proc. Roy. Irish Acad., 1928, **38** A, 18—28).—Mathematical.

Electron in a gravitational field. J. M. Whittaker (Proc. Camb. Phil. Soc., 1928, **24**, 414—420).—Mathematical.
W. E. Downey.

Wave mechanics of an atom with a non-Coulomb central field. III. Term values and intensities in series in optical spectra. D. R. Hartree (Proc. Camb. Phil. Soc., 1928, **24**, 426—437).—Mathematical.
W. E. Downey.

Inversion point of the second order. W. Jazyna (Z. Physik, **49**, 270—278).—Mathematical.
R. W. Lunt.

Impulse-energy-jump in Dirac's quantum theory of electrons. H. Tetrode (Z. Physik, 1928, **49**, 858—864).—Mathematical.
J. W. Smith.

Measurement of light absorption. H. von Halban and J. Eisenbrand (Z. wiss. Phot., 1928, **25**, 138—152; cf. A., 1927, 1017).—The factors for carrying out measurements of light absorption are critically discussed. The advantages and disadvantages of the photographic and the photo-electric methods are considered. With a sufficiently high extinction, the extinction coefficient can be determined photographically with an accuracy of a few per cent. The photographic method is not suitable for determining small differences of extinction or of concentration of absorbing material, or for the absolute measurement of small extinctions ; it is, however, very suitable for the complete quantitative determination of absorption spectra, and for this it is more useful than the photo-electric method owing to its rapidity. The photo-electric method shows no lower limit of differential sensitiveness in regard to extinction, and is therefore eminently suitable for estimating low values of extinction and small differences of extinction. In absolute measurements its sensitiveness cannot be fully utilised. In determining complete absorption spectra the limited number of lines utilisable is a disadvantage. The differences observed between the photo-electric and photographic methods at wave-lengths below λ 3000, and especially with nitrate solutions, are explained by systematic errors in the photo-electric measurements. Photo-electric cells show unexpectedly large differences in the relation of sensitivity to wave-length. The exact knowledge of the properties of the cell used is especially important if absolute measurements are to be made with impure light. W. Clark.

Pleochroism of tourmaline. P. Le Roux (J. Phys. Radium, 1928, [vi], 9, 142—152).—Absorption measurements on two sections of tourmaline cut parallel and perpendicular to the optical axis have been made for the mercury arc lines 5790—3655 Å. using a photo-electric cell and quadrant electrometer. When absorption is no longer small, the coefficient of absorption varies with the direction of propagation of the light, the value being less in the direction parallel than in that perpendicular to the axis of the crystal. This has been confirmed with a second sample of yellow tourmaline. The different value obtained in this case for the coefficient of absorption indicates that the coloration of tourmaline is due to an impurity. L. S. Theobald.

Dielectric constants and absorption indices of ethyl alcohol for short electric waves. S. Mizushima (Proc. Imp. Acad. Tokyo, 1928, 4, 205—207).—The dielectric constant and absorption index of ethyl alcohol were determined at various temperatures between 60° and −60° by the resonance method, using electric waves of wave-length 59 cm. The results so obtained, together with those published previously (cf. A., 1926, 560, 778, 886, 1082) for other wave-lengths, show that the region of anomalous dispersion is shifted towards longer wave-lengths as the temperature is lowered. This agrees with Debye's dipole theory. From the experimental values for the dielectric constant, and by making use of Debye's formula, the molecular radius can be calculated. It is found to be $2{\cdot}1\times10^{-8}$ cm., which is in good agreement with the value obtained by other methods.

A. J. Mee.

Cathode phosphorescence of erbium in calcium oxide. S. Fagerberg (Ann. Physik, 1928, [iv], 86, 435—446).—The emission spectrum of an erbium sulphate phosphor has been observed over the range 6800—3100 Å. and the wave-lengths of some 150 lines and bands have been measured. J. W. Smith.

Metallic reflexion from rock salt and sylvite in the far ultra-violet. A. H. Pfund (Physical Rev., 1928, [ii], 32, 39—43).—The wave-lengths of the true resonance frequencies are estimated to be 1547 and 1581 Å. for sodium chloride and potassium chloride, respectively. A. A. Eldridge.

Relation between molecular constitution and colour. III. Reciprocal influence of the component valency fields of a molecule. Inversion of the absorptive character of two chromogens. M. V. Ionescu (Bul. Soc. Stiinte Cluj, 1927, 3, 373—380; Chem. Zentr., 1928, i, 696—697).—The phenyl, *p*-methoxyphenyl, and 3 : 4-methylenedioxyphenyl derivatives of benzofulvene absorb more strongly than these derivatives of dibenzofulvene, but the absorption intervals are not equal. "The absorption interval of two substances with identical substituents but different chromogens diminishes as the co-ordinatively unsaturated character of the substituents increases." In fact, bis-*p*-dimethylaminophenyldibenzofulvene absorbs more strongly than bis-*p*-dimethylaminophenylbenzofulvene, owing to the reciprocal influence of the valency fields of the chromogen and the substituents. If the co-ordinative unsaturation of the substituents disappears, *e.g.*, by salt formation, the normal absorptive character of the chromogen returns. A. A. Eldridge.

Absorption spectrum of nitric oxide. M. Lambrey (Compt. rend., 1928, 187, 210—212; cf. A., 1927, 808).—The absorption spectrum of nitric oxide has been measured. The formulæ representing the composition of the doublet 2267·85, 2261·5 are, first component, $\nu=44082+10{\cdot}7N+2{\cdot}3N^2$ and $\nu=44077+2{\cdot}3N^2$, second component, $\nu=44196{\cdot}5+9{\cdot}12N+2{\cdot}76N^2$ and $\nu=44200+2{\cdot}76N^2$. The doublet 2153·75, 2148·15 is represented by, first component, $\nu=46419+10{\cdot}2N+2{\cdot}1N^2$ and $\nu=46413{\cdot}5+2{\cdot}1N^2$, second component, $\nu=46536+8{\cdot}72N+2{\cdot}56N^2$ and $\nu=46531{\cdot}5+2{\cdot}56N^2$. C. W. Gibby.

Luminescence of water and carbon disulphide under the influence of γ-rays. L. Mallet (Compt. rend., 1928, 187, 222—223).—Under the influence of γ-rays water and carbon disulphide give rise to continuous luminescence spectra. C. W. Gibby.

Polarisation of infra-red radiation by calcite. A. M. Taylor (Phil. Mag., 1928, [vii], 6, 88—97).—Infra-red radiation has been shown to be partly polarised by passage through thin plates of calcite cut parallel to the optic axis. These polarisation effects have been used to differentiate between the absorption bands of the calcite in the infra-red region due to real maxima of absorption and those which are merely the effect of interference. Six fundamental absorption bands over the range 94—7 μ with a first and second harmonic have been verified. The frequencies measured are in agreement with those calculated by ignoring the assumption of Schaefer (A., 1927, 5) of an inactive frequency which is active in combination. A. E. Mitchell.

Influence of different nuclei on the absorption spectra of organic compounds. J. E. Purvis (Proc. Camb. Phil. Soc., 1928, 24, 421—425).—In the phenyl derivatives of the two naphthylamines it is found that the introduction of the phenyl group produces an additional band; in the *ar*- and *ac*-hydrogen derivatives of these two compounds the type of absorption is controlled by the saturated or unsaturated condition of each constituent ring. In the cresols, the introduction of a nitroso-group produces colour. In the anilides, the position of the typical absorption of aniline is destroyed, and it is replaced by a band due to a phenyl group. W. E. Downey.

Fluorescence of mercury vapour under low excitation. (Lord) Rayleigh (Nature, 1928, **122**, 242).—Radiation of wave-length 3125 Å. excites the green band fluorescence of mercury vapour.

A. A. Eldridge.

Absorption of light by solid and dissolved salts and absorption by ions. H. Ley [with W. Heidbrink] (Z. anorg. Chem., 1928, **173**, 287—296).—The absorptive power of copper sulphate solutions for ultra-violet light between 0·30 and 0·25 μ deviates appreciably from Beer's law; a similar result is obtained with concentrated solutions of copper perchlorate. The absorptive power of the solid pentahydrate is appreciably less than that of the solution, showing that the hydrated ion $[Cu4H_2O]^{\cdot\cdot}$ is present in the crystal lattice and that this forms a more normal and more optically saturated system than does the solution, the deviations in the absorptive power of which are ascribed to the formation of complex anions. The change in the colour of solutions of nickel and copper sulphates produced by the addition of sulphuric acid is shown by examination of the absorption spectrum to be due to dehydration of the coloured cation. A. R. Powell.

Distribution of velocity of the excited sodium atoms produced in the optical dissociation of sodium iodide. A. C. G. Mitchell (Z. Physik, 1928, **49**, 228—235).—The Doppler effect for the *D*-light emitted by excited sodium atoms produced by passing the light from cadmium or zinc arcs through sodium iodide vapour at 650° has been measured in directions parallel and perpendicular to the direction of the beam producing dissociation. Since the effect is sensibly the same in the two directions, it follows that the velocities of the excited sodium atoms in these directions are also equal. R. W. Lunt.

Device for measuring spectrum photographs. R. Frisch (Z. Physik, 1928, **49**, 608).—A simple device is described suitable for the rapid determination of distances separating lines in a spectrum photograph with an accuracy of 0·01 mm. R. W. Lunt.

Structure and activation of the formaldehyde molecule: analysis from the point of view of the ultra-violet absorption spectrum of the vapour. V. Henri and S. A. Schou (Z. Physik, 1928, **49**, 774—826).—The ultra-violet absorption spectrum of formaldehyde vapour has been investigated and 35—40 bands have been located between 3700 and 2500 Å. The absorption maximum is at 2935, as for other aldehydes. The bands can be divided into 11 groups, the first 7 groups containing rotation bands, whilst the other groups are indefinite and continuous and are attributed to the pre-dissociated molecule. A double fine structure was found in the first 7 bands and is explained by assuming a doubly-quantised rotation of the molecule, corresponding with two moments of inertia J and K, the former about the C—O axis of the molecule, and the latter at right angles to it. The values deduced for the moments of inertia of the normal molecule are $J_0=1{\cdot}38\times10^{-40}$, $K_0=23\times10^{-40}$. From this the configuration of the molecule is deduced as of Y-form with the following inter-atomic distances: H—H$=1{\cdot}38\times10^{-8}$ cm.; C—O$=1{\cdot}09\times10^{-8}$; C—H$=1{\cdot}3\times10^{-8}$ cm. Similarly, there are two vibration numbers α and β, corresponding with C—O vibrations and H—H vibrations, respectively. For the normal molecule $\alpha_0=1572{\cdot}3$ and $\beta_0=441$ cm.$^{-1}$, whilst for the excited molecule $\alpha'=1231{\cdot}3$ and $\beta'=398$ cm.$^{-1}$ The band structure shows a triplet system, and the lines in each band can be arranged very exactly according to nine parabolas. The separation of the bands in these triplets is independent of the state of vibration of the atoms and is almost equal to the value calculated from the emission spectrum of the CO molecule. The carbon monoxide molecule is supposed to exist normally in the ^1S state, from which it was predicted that it would have a new absorption band at 2060·6 arising from the $^1S-{}^3P$ change. This was found at 2060·8 Å. The deductions are drawn that the formaldehyde molecule exists normally in the ^3P state and passes through seven successive stages of vibrational activation into a pre-dissociated substance. At higher temperatures the latter condition appears at lower degrees of excitation than at normal temperatures.

Observations of the absorption spectrum of formaldehyde in solution showed that in water the formaldehyde molecule is completely hydrated, whilst in hexane at −70° it remains in the unimolecular state. J. W. Smith.

Optical excitation and dissociation of metallic halides. K. Butkov and A. Terenin (Z. Physik, 1928, **49**, 865—884).—In continuation of previous work (A., 1926, 776; 1927, 1009) the optical dissociation of the cæsium iodide, thallous bromide and chloride, and cuprous iodide molecules into the excited metallic atom and neutral halogen atom has been investigated. The limiting frequencies at which the lines characteristic of the metallic atom are emitted when the vapour of the halide is irradiated with an intense beam of short ultra-violet light were determined, and the heat of dissociation of the molecules so deduced was found to be in satisfactory agreement with those calculated from thermochemical data. In the case of thallous iodide vapour, optical excitation causes the emission of a band spectrum of the TlI molecule besides the atomic lines. From this, the various dissociation processes are related with the energy levels in the molecules. The data obtained are compared with those found previously.

J. W. Smith.

Titanium oxide bands. A. Christy and R. T. Birge (Nature, 1928, **122**, 205).—Each of the blue-green titanium bands consists of three *R* and three *P* branches. The three heads of the 0—0 band lie at 19,349, 19,347, and 19,340 cm.$^{-1}$ (approx.). The bands are ascribed to neutral TiO, and are probably due to a $^3P-{}^3P$ transition; the lower level is assumed to be an excited level of the TiO molecule.

A. A. Eldridge.

Dielectric polarisation of liquids. III. Polarisation of the isomerides of heptane. C. P. Smyth and W. N. Stoops (J. Amer. Chem. Soc., 1928, **50**, 1883—1890).—The densities, refractive indices, and other physical constants of *n*-heptane, its isomerides, and ββδ-trimethylpentane are recorded for 20°. The dielectric constants and densities of *n*-heptane, ββ-dimethylpentane, γ-ethylpentane, and ββδ-trimethylpentane between −120° and +100° are also recorded. These molecules possess no measurable electric moments. Atoms in saturated hydrocarbons may be linked in every possible configuration without causing measurable lack of electric symmetry, although slight differences in the rigidity of the binding electrons can be detected. The electrical symmetry of the molecules gives no evidence of a difference in the electronegativities of the various constituent radicals. S. K. Tweedy.

Specific heats at low temperatures of manganous oxide, manganosomanganic oxide, and manganese dioxide. R. W. Millar (J. Amer. Chem. Soc., 1928, 50, 1875—1883).—The specific heats were measured from 70° to 300° Abs. The specific heat–temperature curves for manganous oxide and manganese dioxide exhibit discontinuities. With the aid of the Debye and Einstein specific heat functions and the third law of thermodynamics the following entropies (in g.-cal./1°) at 25° were calculated: manganous oxide, 14·92; manganosomanganic oxide (Mn_3O_4), 35·73; manganese dioxide, 13·93. The respective free energies, ΔF, are at 25° (g.-cal./mol.): −85,830, −302,800, and −112,600. S. K. Tweedy.

Electric moment of *p*-azoxyanisole. J. Errera (Physikal. Z., 1928, 29, 426—429).—Measurements of the electric moment are held to indicate that the optical anisotropy of *p*-azoxyanisole is due, not to molecular aggregates, but to the molecules themselves. The value obtained for the electric moment is $\mu = 2{\cdot}3\times10^{-18}$. J. W. Smith.

Determination of dipole moments from critical data. J. K. Syrkin (Z. anorg. Chem., 1928, 174, 47—56).—The equation $m = 1{\cdot}66\times10^{-20}T_cP_c^{\frac{1}{4}}$ has been deduced from the equation for the mean energy of two rigid dipoles; m is the moment of the dipole, T_c and P_c are the critical temperature and pressure. The moments of 79 substances have been calculated, and the results are in agreement with the values observed by other workers. Relationships between the dipole moments of similar compounds are discussed; *e.g.*, for homologous series the moment decreases as the number of carbon atoms in the molecule increases. Additive relationships are observable in a number of cases. H. F. Gillbe.

Molecular and atomic volumes. XX. Space occupied by hydrogen in metallic hydrides. W. Biltz (Z. anorg. Chem., 1928, 174, 42—46).—Hydride formation by the alkali, alkaline-earth, and rare-earth metals is accompanied by a reduction to about half its value of the zero mol. volume. The mol. volumes of the rare-earth hydrides class these elements with the alkali and alkaline-earth groups. H. F. Gillbe.

Raman effect. P. Pringsheim (Naturwiss., 1928, 16, 597—606).—Descriptive.

Dependence of refractive index on temperature and density. G. Peters (Ann. Physik, 1928, [iv], 86, 494—510).—An interferometer method of measuring the refractive index of liquids is described. Measurements on liquid hydrogen cyanide have been made, but the results are not of sufficient accuracy to determine which of the various theoretical formulæ most accurately represents the effect of temperature and density. W. E. Downey.

Rotation polarisation of electromagnetic waves due to tetrahedral molecule models. K. F. Lindman (Acta Acad. Åboensis Math. phys., 1927, 4, No. 1, 1—22; Chem. Zentr., 1928, i, 1146).—Experiments were carried out with isotopic three-dimensional systems of numerous small tetrahedral molecule models and waves of length greater than those of the resonators and the dimensions of the single models. In accord with Biot's corresponding law for optical activity, the rotation of the plane of polarisation of the electromagnetic waves is proportional to the number of molecule models in their path, *i.e.*, to the cross-section of the active substance. A. A. Eldridge.

Polarisation of scattered light quanta. C. V. Raman and K. S. Krishnan (Nature, 1928, 122, 169).

New phenomenon in the scattering of light by crystals. G. Landsberg and L. Mendelstam (Naturwiss., 1928, 16, 557—558).—While investigating the scattering of light, using a mercury arc source, from quartz crystals, a diminution in frequency of the scattered lines 2536, 3126, and 3650 Å. was observed. It is suggested that the observed diminution in frequency can be accounted for by the emission of one quantum of an infra-red frequency per quantum scattered, since in the cases recorded the diminution in frequency corresponds with emission at the known absorption region $\lambda = 20{\cdot}7\ \mu$. R. W. Lunt.

Refractive index for electron waves. L. Rosenfeld and E. E. Witmer (Z. Physik, 1928, 49, 534—540).—A theoretical discussion of the relationship between the values of μ, the "refractive index" of a metal, e, the potential in the metal, and V derived from the equation $eV = \frac{1}{2}mv^2$, for various metals.

Valency chemistry of boron, and the constitution of the simplest boron hydride. E. Wiberg (Z. anorg. Chem., 1928, 173, 199—221).—An electronic formulation of boron hydride, B_2H_6, is derived by postulating that (1) the octet rule is valid for boron compounds, (2) the boron atom cannot combine by covalencies with more than 4 atoms, (3) hydrogen is combined by electrovalencies only in the metallic hydrides, and in all other cases by covalencies. The conclusion is reached that in all electrovalency compounds boron is tervalent and in all covalency compounds, quinquevalent. Quadrivalent boron, in the sense of quadrivalent carbon, does not exist. The formula derived is consistent with addition of sodium and ammonia to the hydride, its reactions with water and the hydrogen halides, and the formation of hypoborates. H. F. Gillbe.

Polar conception of co-ordinated valencies. E. J. W. Verweg (Chem. Weekblad, 1928, 25, 250—254).—It is contended that the so-called co-ordinated valencies in complex compounds are in fact polar in nature, although "deformed" to such a degree as to appear to some extent non-polar. S. I. Levy.

Structure of thin films. XI. Oxygenated derivatives of benzene. N. K. Adam (Proc. Roy. Soc., 1928, A, **119**, 628—644; cf. A., 1926, 348).—With the object of obtaining films of substances containing the benzene nucleus lying flat on the surface of water, neighbouring rings being in contact with one another, so that the cross-section of the benzene ring parallel to the plane of the ring could be measured, the surface films of a number of resorcinol and phloroglucinol derivatives, all with long side-chains, have been investigated. No films of the required type were obtained. In most of the polyhydroxy-compounds the rings stood upright, whilst in compounds containing methoxyl groups, although the rings probably did lie flat, the films were of the "expanded" type and the orientation and packing were greatly influenced by lateral compression. The cohesional force between film molecules is discussed. Hydroxyl groups greatly increase the lateral attraction between the rings packed vertically in the films. The carbonyl groups of acyl side-chains in the polyhydroxy-compounds also appear to increase the lateral attraction, but in the polymethoxy-compounds the carbonyl groups in the side-chains appear to come into contact with the water and increase the area. The compound ωω'-bis-2 : 4-dihydroxyphenyldecane forms gaseous films with the molecules lying flat, in accordance with the rule that two widely separated points of attachment to the water on the chain cause the molecules to lie flat and the films to become gaseous. The lateral attraction between the flat molecules in these gaseous films is diminished by acetylating the hydroxyl groups, and the area of the molecule is measured. Humulon (cf. Wieland, Martz, and Hock, A., 1925, i, 1422) forms a film of unique type in which the ring is probably flat on the water and in contact with adjacent rings. Although the film is of the required type, however, the substituents in the molecule are too numerous for any idea of the true cross-section of the benzene nucleus to be obtained.

L. L. Bircumshaw.

Energy distribution of complex molecules. O. K. Rice (Physical Rev., 1928, [ii], 32, 142—149).—Theoretical. The distribution over a range of energies for a given average energy of the molecules over a range of temperatures is formulated and the results are applied to the decomposition of azomethane.

A. A. Eldridge.

Kinetics of absorption of ultra-sonic waves. D. G. Bourgin (Nature, 1928, **122**, 133).—The attenuation of ultra-sonic waves in passing through carbon dioxide, hydrogen, or helium, and the accompanying frequency variation of velocity are correlated with the mechanisms of collisions of the first and second kinds.

A. A. Eldridge.

Form of molecules of cellulose and polymerised substances. J. R. Katz and P. J. P. Samwel (Naturwiss., 1928, **16**, 592—593).—A new method has been worked out by which unimolecular surface films can be prepared by spreading chloroform solutions on water. Examination of films derived from crystalline cellulose derivatives and technical preparations of high and low viscosity gave sensibly equal values for the thickness and the area per $C_6H_{10}O_5$ unit. Since the layers are only one to two carbon atoms thick, the aggregates must be in the form of threads or leaves, formed by polymerisation in one or two dimensions only. Probably, from other evidence, the former is the case. Other polymerised substances (anethole, vinyl acetate, and methyl acrylate) gave analogous results.

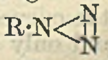
R. K. Callow.

Chemical interactions corresponding with the constant of mass action being a function of the volume and masses of the constituents as well as of the temperature and catalytic action. R. D. Kleeman (Phil. Mag., 1928, [vii], 6, 195—203).—By extending his previous results (this vol., 263, 470, 955) the author shows that a dense substance in contact with reacting gases of which it may occlude one or more, to any extent, renders the constant of mass action a function of the volume and masses of the constituents. Thus in addition to affecting the velocities of the changes occurring in the reacting mixture, a catalytic agent can also affect the value of the mass action constant to an extent depending on the volumes and masses of the constituents of the reacting mixture.

A. E. Mitchell.

Rate of vibration and molecular packing of organic compounds. W. Herz (Z. anorg. Chem., 1928, **173**, 358—360).—If v is the rate of vibration and z the number of molecules in unit volume just above the m. p., it is shown for about thirty organic liquids that the ratio $z^{4/7}/v$ is a constant which is approximately 3. For the hydrocarbons ethane to decane the results recorded vary from 3·02 to 3·75, for the corresponding primary alcohols from 2·90 to 3·08, and for various fatty acids and aromatic hydrocarbons from 2·77 to 3·28. Hydrogen cyanide, however, gives a value of 1·82 and iodobenzene 4·14.

A. R. Powell.

Constitution of azoimide and its esters. H. Lindemann and H. Thiele (Ber., 1928, **61**, [*B*], 1529—1534).—Determinations of the parachor of a number of derivatives of azoimide show that Thiele's formula, R·N:N⋮N, for these compounds and hence probably for azoimide is untenable. The assumption is thereby made that the double linking between the nitrogen atoms has the same value as the C:C, C:O, C:S, or N:O linkings, and the triple linking the same effect as the acetylenic or C⋮N linking. The calculated values for the cyclic form  agree excellently with the observed data. The following figures are recorded: ethyl azidoacetate, b. p. 74°/18 mm., d_4^{19} 1·1263, γ 34·11; azidoacetone, b. p. 71°/18 mm., $d_4^{18\cdot5}$ 1·1228, γ 39·33; phenyl azide, b. p. 80°/30 mm., $d_4^{21\cdot5}$ 1·0959, γ 36·66; *o*-tolyl azide, b. p. 88°/23 mm., $d_4^{22\cdot2}$ 1·0709; γ 35·73; *p*-tolyl azide, b. p. 85°/22 mm., $d_4^{22\cdot5}$ 1·0527, γ 34·78.

H. Wren.

Magnetic resolution of bismuth vapour streams. A. Leu (Z. Physik, 1928, 49, 498—536).—The magnetic resolution of streams of bismuth vapour has been investigated at temperatures in the range 1090—1430°. At the lower end of this range there is a considerable undeflected beam thought to be due to Bi_2 molecules; this disappears completely at 1430°. The observed resolution corresponds with a magnetic moment μ_1 of $0{\cdot}72_3$ Bohr unit in qualitative agreement with theory; the value of μ_1 is independent of the resolving field strength. From measurements of the temperature variation of the intensity of the undeflected beam it is shown that an approximately linear relationship exists between the dissociation constant for bismuth ($Bi_2=2Bi$) and the reciprocal of the absolute temperature. The corresponding value of the heat of dissociation of the Bi_2 molecule is $6\pm1{\cdot}5\times10^4$ g.-cal., whilst the value calculated by the Nernst heat theorem on analogy with iodine is $5{\cdot}6\times10^4$ g.-cal.

R. W. Lunt.

Newer measurements in the *L*-series of *X*-ray spectra. H. Brauns (Z. wiss. Phot., 1927, **25**, 325—344).—In *X*-ray spectroscopy, measurements of wave-length are "absolute" if they depend on the lattice constants of a crystal, which are given by the formula $d=(MeE/2\rho VSC)^{1/3}$, where M is mol. wt., e the elementary electric charge, E the equivalent wt., ρ the density of the crystal, V the volume of the elementary crystal cell, S the at. wt. of silver, and C the velocity of light. This, however, gives results correct to four figures only, whereas spectroscopic measurements are accurate to six. Moseley's calculated figure for the constants of rock salt are therefore arbitrarily accepted as standard. In "relative" measurements the lines are referred to a standard line, usually the $K\alpha_1$ line of copper, but owing to the small degree of regularity among the lines of the *X*-ray spectrum, a number of secondary reference lines at intervals of 50X are necessary. As the value for the copper line is uncertain within 1%, a table is given to facilitate conversion of the value of a line from one standard into another.

Bragg's turning crystal method and Seemann's camera method have been modified by Siegbahn to give absolute measurements. The former overcomes the difficulty due to the non-parallelism of the *X*-radiation, but as it is impossible to distinguish completely the images due to the first and the subsequent layers in the crystal, it has been largely replaced by the second method. In both cases the net error is of the order 0·05 Å.

The "relative" method was used here, the substance to be investigated being rubbed on to a copper anticathode. A film was used instead of a plate so as to fit the curved chamber. Exposure required $1\frac{1}{2}$—3 hrs., and only the $L\alpha_1$ lines were taken to sufficient intensity. The results are as follow (X): tantalum 1518·79; tungsten 1473·37; lead 1172·55; bismuth 1141·55; uranium 908·96. Except in one or two cases these agree within experimental error with the results of other workers.

S. J. Gregg.

Diffraction of cathode rays. II. G. P. Thomson (Proc. Roy. Soc., 1928, **A**, **119**, 651—663).—A continuation of previous work (cf. this vol., 3). Using a modified apparatus, diffraction patterns have been obtained by passing a beam of cathode rays through thin films of platinum, and the results are in complete agreement with the de Broglie theory of electron waves. The values of the crystal constants of aluminium, gold, and platinum, found by applying the de Broglie theory, agree to 1% with those determined by *X*-ray analysis. Evidence is obtained which indicates that the electrons must be accompanied by a train of not less than 50 waves in length.

L. L. Bircumshaw.

Diffraction of cathode rays by thin celluloid films. A. Reid (Proc. Roy. Soc., 1928, **A**, **119**, 663—667; cf. preceding abstract).—The diffraction patterns obtained are in complete agreement with those predicted by the de Broglie wave theory. The energy of the ray was measured by electrostatic deflexion, and the results agree to 1% with those obtained by Thomson (preceding) where the energy was measured by spark-gap. A possible structure for the celluloid films is suggested.

L. L. Bircumshaw.

Diffraction of cathode rays by thin films of copper, silver, and tin. R. Ironside (Proc. Roy. Soc., 1928, **A**, **119**, 668—673).—Results in agreement with the de Broglie wave theory have been obtained by observation of the diffraction patterns formed on passing electrons through thin films of copper, silver, and tin, using the apparatus and method described by Thomson (preceding). The values of the grating constants, calculated on the de Broglie theory, agree to about 1% with those determined by *X*-ray analysis.

L. L. Bircumshaw.

Critical-absorption photometer for the study of the Compton effect. C. V. Raman and C. M. Sogani (Proc. Roy. Soc., 1928, **A**, **119**, 526—530).

New method of *X*-ray spectroscopy. Orientation of fatty acids on mercury. J. J. Trillat (Compt. rend., 1928, **187**, 168—169).—Satisfactory spectra can be obtained by using a drop of mercury covered with a very small quantity of fatty acid, melting the latter if solid. By this means orientation at liquid–liquid and liquid–solid interfaces can be investigated. It persists up to at least 100°.

C. W. Gibby.

Absorption of *X*- and γ-rays and the secondary radiations which accompany them. Duc de Broglie (Brit. J. Radiol., Roentgen Soc. Sect., 1927, **23**, 55—62).—A discussion of absorption, ionisation, and therapeutic effect. Chemical Abstracts.

Relative intensities of *X*-ray lines in the *L*-spectrum of uranium. S. K. Allison (Physical Rev., 1928, [ii], **32**, 1—11).—The relative intensities of 17 lines in the *L*-spectrum of uranium have been studied, and the results extrapolated to voltages greater than the critical. A. A. Eldridge.

Interpretation of atomic structure factor curves in crystal reflexion of *X*-rays. G. E. M. Jauncey and W. D. Claus (Physical Rev., 1928, [ii], **32**, 12—21).—Previous work (this vol., 692) is continued. For any atom *F*-values, calculated according to the classical theory and unmodified for the Compton effect but multiplied by the Debye temperature factor, give *U*-curves the areas under which never exceed the number of electrons assumed in the model. For certain values of *D*, the grating space of a crystal of rock salt, both experimental and modified theoretical *F*-values give *U*-curves the areas under which exceed the true number of electrons.

It appears that the Compton effect is involved, and that the present Fourier analysis method is invalidated. A. A. Eldridge.

Scattering of *X*-rays from gases. C. S. Barrett (Physical Rev., 1928, [ii], **32**, 22—29).—Carbon dioxide, argon, oxygen, nitrogen, and helium, but not hydrogen, show excess scattering of molybdenum *X*-rays; the effect is largely due to interference arising within the atom. The effect with helium may be due to the presence of nitrogen.

A. A. Eldridge.

Anomalous dispersion in the *X*-ray region. R. Forster (Naturwiss., 1927, **15**, 969—970; Chem. Zentr., 1928, i, 642).—Determinations of n for *X*-rays in the region of an absorption edge give results at variance with the theories of Lorentz and of Kallmann and Mark. A. A. Eldridge.

Is crystal reflexion of *X*-rays entirely a classical phenomenon? I. Waller and R. W. James (Nature, 1928, **122**, 132—133).

Index of refraction of glass for *X*-rays of long wave-length. J. Thibaud (Compt. rend., 1928, **187**, 219—221).—The limiting angle of total reflexion by glass of *X*-rays of wave-lengths between 1·5 and 65 Å. has been measured. As the absorption of the rays increases as the cube of the wave-length, the refractive index diminishes by an amount proportional to the square of the wave-length.

C. W. Gibby.

Multiple ionisation and the absorption of *X*-rays. F. K. Richtmyer (Phil. Mag., 1928, [vii], **6**, 64—88).—The possible existence of *X*-ray absorption spectra discontinuities corresponding with satellites analogous to the K, L, M, etc. discontinuities in *X*-ray spectra of the first order is discussed and it is concluded that the processes giving rise to the satellites are secondary and evidence concerning them is not to be expected in absorption spectra. Such evidence is difficult to deduce, since the satellites are weak in comparison with the parent lines and existing data on *X*-ray absorption coefficients are not sufficiently precise to demonstrate possible discontinuities. Since the square root of the difference in frequency between a satellite and its parent is directly proportional to the atomic number of the element emitting them it is suggested that the satellites arise from two-electron transfers. The importance of obviating the "slit width" error in precise measurements of *X*-ray absorption coefficient is demonstrated and it is shown that some of the published data in the region of 0·3 Å. must be several per cent. in error from this source alone.

A. E. Mitchell.

Atomic scattering power for *X*-rays from powders of gold, silver, and aluminium for Cu-*Kα* radiation. J. Brentano (Phil. Mag., 1928, [vii], **6**, 178—191).—In order to eliminate effects due to the absorption coefficient and other constants depending on the particular conditions of the measurement the comparative intensities of reflexion from different crystals have been determined under simplified conditions by working with a composite powder comprising the substance under examination and a reference substance of appreciably greater lattice constant. Cadmium oxide is a suitable reference substance for the examination of gold, silver, and aluminium. A method of interpreting the photographic results is described. The results indicate that for the elements of high at. wt. examined in the state of very fine powders the scattered intensity is practically proportional to the effective negative atomic change and not to the square of this quantity as required by the theory of Darwin and others.

A. E. Mitchell.

Statistical derivation of the *M*-terms of the *X*-ray spectrum. F. Rasetti (Z. Physik, 1928, **49**, 546—549).

Structure of mercerised cellulose. I. Space lattice of mercerised ramie cellulose as developed from *X*-ray data. O. L. Sponsler and W. H. Dore (J. Amer. Chem. Soc., 1928, **50**, 1940—1950).—*X*-Ray diffraction data indicate that there is a critical concentration of sodium hydroxide, about 13%, above which cellulose fibres become mercerised; mercerisation is not a progressive change (Herzog, A., 1926, 677). The elementary cell of mercerised cellulose is slightly monoclinic and contains two $C_6H_{10}O_5$ units; the axes are $a=4\cdot53$, $b=7\cdot61$, and c (long axis of fibre)$=10\cdot30$ Å. Comparison with the lattice of unmercerised cellulose (Sponsler, A., 1926, 760) shows that mercerisation has caused a to decrease and b to increase, and the angle between these axes to change from 90° to 83°. Mercerisation appears to be the result of rearrangement in three different ways, viz., shift in the position of the chain with respect to the neighbouring chains, a partial rotation of the alternate glucose units in each chain (the latter remaining intact), and a shift in the position of the hydroxyl group attached to the sixth carbon atom, thus rendering it unlikely that mercerisation involves any type of molecular rearrangement of the constituent glucose (cf. Katz and Mark, B, 1925, 495). The results support a cellulose structure made up of continuous chains of glucose units held together by primary valencies, mercerisation being capable of overcoming only the secondary valencies (cf. Meyer and Mark, this vol., 621). S. K. Tweedy.

Microstructure of ferrite. H. S. Rawdon and T. Berglund (U.S. Bur. Standards Sci. Papers No. 571, 1928, **22**, 649—717).—The microstructure of ferrite in re-melted electrolytic iron, open-hearth iron, and wrought iron has been investigated. Three types of structure, α, γ, and δ, are noted, associated with the three allotropic forms. α-Veining appears as a branching network within the α grains, but the size of the latter is unaffected. It is independent of the size of the ingot, and may be produced in abundance by forging at or just below the α–γ transition temperature. It has no effect on the mechanical properties of the ferrite. The δ network, a coarse network superimposed on the α grain pattern, consists of minute inclusions, and is connected with "hot-shortness." The γ network, which has no appreciable effect on the mechanical properties, also depends on minute inclusions, and is produced by heating for some time above the α–γ transition temperature. α-Veining can be suppressed by adding silicon, but not by aluminium or manganese. C. W. Gibby.

Pleochroic haloes in biotite from near Murray Bay, P.Q. D. E. Kerr-Lawson (Univ. Toronto Studies, Geol. Ser., Contrib. Can. Min., 1927, No. 24, 54—70).—The distribution of the haloes suggests that the nuclei were formed after crystallisation and rupture of the mica. The haloes consist of shells of darkened mica, separated by lighter shells in which a bleaching or lightening effect is active. The first effect of rays from radium-*C* is to lighten the biotite. Chemical Abstracts.

Crystal structure of certain aromatic compounds. W. H. Bragg (Z. Krist., 1927, **66**, 22—32; Chem. Zentr., 1928, i, 638).—A study of the relative intensities of reflexion at various planes in anthracene indicates that the molecule is of a form containing two periodicities, one being twice as great as the other. Naphthalene tetrachloride has *a* 7·88, *b* 10·30, *c* 14·20 Å., β 112° 40′, with four molecules in the unit cell. 1-Chloronaphthalene tetrachloride has *a* 8·245, *b* 10·1, *c* 15·78 Å., β 116° 12′; naphthalene tetrabromide has *a* 10·75, *b* 8·97, *c* 13·25 Å., β 112° 57′, with four molecules in the unit cell. A. A. Eldridge.

Structure of iron nitride, Fe_4N. R. Brill (Naturwiss., 1928, **16**, 593—594).—Contrary to the conclusions of Hägg (this vol., 605), the *X*-ray examination of an iron nitride, Fe_4N, gives definite evidence of regular spacing of the nitrogen atoms, and, therefore, of the existence of a compound. Less probably the absorption of nitrogen by iron can be regarded as an infiltration of nitrogen atoms into the iron space-lattice with minimal disturbance of the latter and a saturation-limit at the composition Fe_4N. R. K. Callow.

Allotropic form of silver. G. Allard (Compt. rend., 1928, **187**, 223—225).—Silver obtained by the action of copper on a solution of silver nitrate does not possess the usual cubic structure. The unit cell is an orthorhombic prism of height $4·23\times10^{-8}$ cm., the sides of the base being $3·76\times10^{-8}$ cm., inclined at 81° 30′ to one another. C. W. Gibby.

Crystal structure of cryolithionite. G. Menzer (Fortschr. Min. Kryst. Petr., 1927, **12**, 58—59; Chem. Zentr., 1928, i, 1359).—The structure of cryolithionite, $Na_3Li_3Al_2F_6$, is similar to that of granite. The lattice constant is $12·10\pm0·025$ Å. The space-centred lattice contains eight molecules; the space-group is O_h^{10}; $d_{calc.}$ is $2·79\pm0·02$. A. A. Eldridge.

***X*-Ray fine structure of cyanite and staurolite.** G. M. Cardoso (Fortschr. Min. Kryst. Petr., 1927, **12**, 18—20; Chem. Zentr., 1928, i, 1359).—Cyanite (with rhombic pseudo-symmetry) has a_0 7·122, b_0 7·883, c_0 5·650 Å., with four molecules in the unit cell; d_{100} 6·717, d_{010} 7·575, d_{001} 5·530 Å.; on transformation a_0' 26·868, b_0' 7·883, c_0' 5·650 Å., with 16 molecules in the unit cell. A. A. Eldridge.

***X*-Ray fine structure of brookite; physical properties of the three titanium dioxides.** A. Schröder (Fortschr. Min. Kryst. Petr., 1927, **12**, 83—84; Chem. Zentr., 1928, i, 1359).—The unit cell contains eight molecules having d_{100} $9·136\pm0·020$, d_{010} $5·439\pm0·010$, d_{001} $5·153\pm0·020$ Å. A. A. Eldridge.

Structure of benitoite. J. J. P. Valeton (Fortschr. Min. Kryst. Petr., 1927, **12**, 91—92; Chem. Zentr., 1928, i, 1359).—Benitoite, the only representative of the ditrigonal–bipyramidal class, has *a* 6·64, *c* 9·71 Å., *a* : *c* 1·4634, with two molecules of $BaTiSi_3O_9$ in the unit cell, and space-group D_{3h}^2 or D_{3h}^4. A. A. Eldridge.

Crystal structure of tetramethylammonium iodide. W. Zachariasen (Norsk geol. Tidsskr., 1927, **10**, No. 1, 9 pp.; Chem. Zentr., 1928, i, 1360—1361).—The edge of the unit cell of tetragonal tetramethylammonium iodide is 5·76, and $a=8·03$ Å. The unit cell contains two molecules. Alternative positions of the nitrogen atoms in the space-group D_{4h}^7 are possible, but cannot be differentiated by consideration of the intensity of reflexion, although chemical relationships indicate one. Vegard's results (A., 1917, ii, 296) are criticised. The ammonium ion is considered to possess spherical symmetry, whereas the symmetry of the phosphonium, trimethylammonium, and trimethylphosphonium ions is considered to deviate from spherical. A. A. Eldridge.

Evidence obtained by *X*-ray analysis of films of iron in magnetic fields as to the ultimate nature of magnetism. T. D. Yensen (Physical Rev., 1928, [ii], **32**, 114—123).—The most minute crystal aggregates in films of electrolytic iron are not oriented in a magnetic field. The result supports the view that the ultimate magnetic particle is an intra-atomic unit. A. A. Eldridge.

[Electrical conductivity of] silicates. E. Cherbuliez and P. Rosenberg (Helv. Chim. Acta, 1928, **11**, 731—750).—The chemical changes occurring in silicates have been followed by measurements of electrical conductivity at 800—1200°. The conductivity of orthoclase at approximately 800° increases markedly with the duration of heating, reaching a limiting value for a definite temperature. Cooling and re-heating to the same temperature have no further effect on the conductivity, but successive increments of temperature are accompanied by similar variations in conductivity. Albite and leucite, but not nepheline, behave similarly. The increase in conductivity is explained by a dissociation of orthoclase or albite with rising temperature into silica and a silicate poorer in silica, probably of the type of nepheline. The reaction follows the unimolecular law and its reversibility is shown by a diminution in conductivity consequent on heating a mixture of nepheline and quartz at 900—1000°. With the technique used, the polymeric changes undergone by quartz on heating or the chemical changes occurring in kaolin could not be followed. L. S. Theobald.

Magnetic moments of the cupric ion. F. Birch (J. Phys. Radium, 1928, [vi], **9**, 137—141).—A thermomagnetic study of cupric chloride and sulphate has been made at various temperatures. The chief magnetic moment of the cupric ion is 10 magnetons, but one of 9 was observed in a solution of cupric chloride, and the intermediate values obtained in certain cases suggest one of 11. All the cases studied followed the law of Weiss, with the exception of anhydrous copper sulphate between 100°

and 500°, and of cupric oxide which shows a steady paramagnetism. L. S. THEOBALD.

Magnetic susceptibilities of electronic isomerides. II. S. S. BHATNAGAR and R. N. MATHUR (Phil. Mag., 1928, [vii], **6**, 217—223).—The empirical equation of Bhatnagar and Dhawan (this vol., 454) has been modified to conform more closely with Langevin's theory of atomic diamagnetism. The equation becomes $x_m=-2{\cdot}86\times10^{10}\times2/3KR^2$, where x_m is the molecular diamagnetic susceptibility, K is an arbitary constant, and R is the molecular radius calculated over only part of electron orbits, as required by the general application of Langevin's theory, the extent of which is given by the value of K. Tests on a number of compounds show the general application of the revised equation and indicate that the values of K increase with the number of atoms in the molecule; for every two isomeric molecules K is the same, and in the case of groups of isomerides having the same number of atoms in the molecule the values of K increase with the atomic numbers of the groups. A. E. MITCHELL.

Existence of two magnetic rotatory powers for a uniaxial crystal along and normal to the axis. J. BECQUEREL (Compt. rend., 1928, **187**, 215—217).—The magnetic rotatory power of tysonite, the birefringence of which is very small, has been investigated for the green mercury line 5460·7 Å. The rotatory power in the direction of the axis is different from that normal to it. A formula is deduced on theoretical grounds which is in agreement with the results. C. W. GIBBY.

Influence of boric acid on the dispersion of optical glasses in the near infra-red. T. DREISCH and P. LUEG (Z. Physik, 1928, **49**, 380—385).—The refractive index to six significant figures has been determined for a number of optical glasses, with and without a boric acid content, in the range 0·5—2·5 μ; the difference between the index for 1·47 and 2·39 μ is approximately proportional to the boric acid content. R. W. LUNT.

Sulphur and selenium. E. KORINTH (Z. anorg. Chem., 1928, **174**, 57—60).—Two new modifications of sulphur are described in detail, viz., ζ-sulphur (rhombic plates), which is colourless and exhibits weak double refraction, and η-sulphur (hexagonal plates), which is almost colourless and doubly refracting. Both forms are more stable than δ-sulphur. Investigations of the modifications of selenium are described. H. F. GILLBE.

Physical properties of platinum. A. G. GRIGORIEV (Ann. Inst. Platine, 1928, **6**, 178—183).—Values obtained by various authors for the electroconductivity of platinum, its hardness, and tensile strength are compared, and shown to be very close to the corresponding figures found for Russian commercial platinum. R. TRUSZKOWSKI.

Mol. heat and entropy of hydrogen chloride calculated from band spectra data. E. HUTCHISSON (J. Amer. Chem. Soc., 1928, **50**, 1895—1900).—The mol. heats of hydrogen chloride from 1° to 000° Abs. are calculated on the basis of Kemble's values for the energy levels, using the newer quantum mechanics. The plot of the mol. heat against the temperature passes through a maximum at 12·5° Abs. The entropies are calculated by the method of Giauque and Wiebe (this vol., 228). At 0° the entropy is 44·04 or 43·72 g.-cal./1° per mol., according as the Tetrode or Lewis equation is used. S. K. TWEEDY.

Chemical constants and the new quantum statistics. G. E. GIBSON and W. HEITLER (Z. Physik, 1928, **49**, 465—472).—Mathematical. R. W. LUNT.

Boiling points of the normal paraffins at different pressures. S. YOUNG (Proc. Roy. Irish Acad., 1928, **38**, B, 65—92).—The b. p. of the normal paraffins from methane to pentatriacontane, $C_{35}H_{72}$, are calculated at various pressures from 11 to 19,950 mm. by three different methods. The first method makes use of Young's formula $\Delta=A/T^{B\sqrt{T}}$, where Δ is rise of b. p. per CH_2 group, T is b. p. Abs., and A and B are constants. It was found by using the data available that the values of Δ were reproduced with fair accuracy by the above formula when $\log A=1{\cdot}92251+0{\cdot}026187\log p+0{\cdot}013987(\log p)^2+0{\cdot}0013374(\log p)^3$, and $B=0{\cdot}01676-0{\cdot}000795\log p$, where p is the pressure. From this formula the b. p. of the paraffins were calculated, for the higher paraffins up to pressures of 30 mm., and for the lower up to 19,950 mm. The method cannot be relied on to give accurate values for the first two or three members of the series. In the second method, the equation $\log T=a+b\log n+c(\log n)^2+d(\log n)^3$ was used, the constants being calculated for the various pressures from data where available for paraffins up to nonadecane, and in other cases up to octane. In the case where there are not so many paraffins under investigation, *i.e.* for pressures above 30 mm., the last term in the equation is dropped. The b. p. of the paraffins were calculated by this method for the same pressures as in the first. The third method makes use of Ramsay and Young's equation, which is put in the form $T_A'/T_B'=a+bT_A'$, where T_A', T_B' are the absolute temperatures at which the vapour pressures of two nearly related compounds are equal, and a and b are constants. It was found necessary to add a further small term to the right-hand side of the equation in the case of the paraffins. By taking hexane as standard and calculating the constants from available data, the b. p. of the paraffins at various pressures can be calculated. The values given by the three methods are compared with the observed values and the probable b. p. is given in each case. The observed b. p. of ethane agree very well with those calculated by the third method, but are very much higher than those obtained by the other methods. It appears that either ethane has not yet been prepared in a pure state, or else its behaviour is exceptional. The observed b. p. of nonadecane are erratic, and mostly too low. The evidence is in favour of the b. p. of the higher paraffins as determined by Francis (cf. A., 1926, 816). A. J. MEE.

Density of anhydrous chromic chloride and its adsorption of water vapour from the atmosphere. M. CRESPI (Anal. Fís. Quím, 1928, **26**, 152—163).—Thirty-four determinations of the density of various forms of anhydrous chromic chlorides have been made, and it is shown to be a unitary substance having a marked power of adsorption of water vapour, which renders it difficult to obtain consistent figures for the density. In a desiccator over sulphuric acid all the water is not lost; the anhydrous salt, obtained by heating at 100° in a current of dry air, has d 2·916. The mol. volume of the adsorbed water increases with the quantity of water retained by the salt. The velocity of adsorption shows the process to be analogous to that of the adsorption of gases by glass surfaces. H. F. GILLBE.

International Bureau of Physico-Chemical Standards. III. Physical constants of 20 organic compounds. J. TIMMERMANS and F. MARTIN (J. Chim. phys., 1928, **25**, 411—451).—The following data for the b. p., m. p., and d^0 have been determined: n-hexane, 68·80°, −95·1°, 0·67704; n-octane, 125·80°, −57°, 0·71845; n-butylbenzene, 183·10°, −81·2°, 0·87695; bromoform, 149·55°, 8·05°, 2·90350 (15°); ethyl iodide, 72·30°, −111·1°, 1·98065; ethylene dichloride, 83·5°, −35·5°, 1·28164; *iso*propyl chloride, 34·8°, −147·0°, 0·8869; *iso*propyl bromide, 59·35°, −89·0°, 1·34715; *sec.*-butyl chloride, 68·25°, −131·3° (racemic), −140·0° (active), 0·87556 (racemic), 0·89497 (active); *iso*butyl bromide, 91·4°, —, 1·29410; n-butyl alcohol, 118·0°, −90·2°, 0·82472; *iso*butyl alcohol, 108·1°, —, 0·81707; *sec.*-butyl alcohol, 99·5°, —, 0·82275 (active), 0·82273 (racemic); ethyl ether, 34·6°, −116·3°, 0·73622; n-amyl ether, 187·5°, −69·3°, 0·79881; methylal, 42·3°, −105·0°, 0·88545; acetone, 56·2°, —, 0·81250; methyl ethyl ketone, 79·6°, −86·6°, 0·82555; ethylene chlorohydrin, 128·6°, −67·5°, 1·22310; carbon disulphide, 46·25°, −116·8°, 1·29270. Data are also given for the variation of b. p. with pressure, the density at various temperatures, coefficients of expansion, refractive indices and dispersive powers, mol. refractions, and viscosities. The results obtained by earlier investigators are given for comparison. H. F. GILLBE.

Validity of the gas laws. W. HERZ (Z. Elektrochem., 1928, **34**, 360—362).—At the critical temperature the volume of 1 g. of a substance calculated from the simple gas laws is about 3·75 times the experimentally determined figure. At $0·9T_c$ the ratio is about 1·45, whilst at $2/3T_c$ the two values are practically identical. These figures for the quantitative deviation from the gas laws are independent of the nature of the substance. H. F. GILLBE.

Densities of liquid elements. L. H. BORGSTRÖM (Finska Kemistamfundets Medd., 1927, **36**, 76—81; Chem. Zentr., 1928, i, 1254).—A comparison.

A. A. ELDRIDGE.

Atomic volume relations in certain isomorphous series. II. A. F. HALLIMOND (Min. Mag., 1928, **21**, 480—484; cf. this vol., 107).—Mol. volumes of salts of calcium, strontium, and barium and of oxygen, sulphur, selenium, and tellurium are tabulated and compared. It is shown that the ratio of the differences (Ba—Ca)/(Sr—Ca) and (Te—S)/(Se—S) is a constant in each case. The atomic volumes are then calculated. L. J. SPENCER.

Changes in the specific gravity of copper and silver [after heat treatment]. R. RUER and J. KUSCHMANN (Z. anorg. Chem., 1928, **173**, 262—267).—Repeated heating of silver and copper alternately in a vacuum and in hydrogen causes a rapid and progressive decrease in the value of d; with copper a decrease of 6% was obtained after several repetitions of this treatment. This phenomenon is attributed to adsorption of hydrogen, followed by expulsion of the adsorbed gas on subsequent heating in a vacuum with consequent swelling of the metal and the formation of internal voids. A. R. POWELL.

Physico-chemical investigations of ordinary and uranium lead chloride. W. A. ROTH and O. SCHWARTZ (Ber., 1928, **61**, [*B*], 1539—1545).—The values d_4^{18} 5·909±0·001 and 5·884±0·001 are found for ordinary lead chloride and uranium lead chloride (Pb=206·05), respectively, from which the identical molecular volumes, 47·07 c.c., are calculated. In solution in water the molecular volumes are identical, whereas differences are observed between the densities of the saturated solutions. The increases in the refractive index of water caused by addition of equal amounts of the two salts differ somewhat, whereas the molecular refractions of the dissolved salts are identical. The equivalent conductivities of the almost saturated solutions are practically equal. The heats of precipitation as chromates are identical.

H. WREN.

Accurate method for comparing the compressibilities of gases below atmospheric pressure. C. G. ADDINGLEY and R. WHYTLAW-GRAY (Trans. Faraday Soc., 1928, **24**, 378—387).—A new differential method for the measurement of compressibility has been developed and has been applied to determine the ratio of the compressibility coefficients of oxygen and hydrogen. The ratio found is 1·00148.

L. F. GILBERT.

Effect of temperature on the viscosity of neon. R. S. EDWARDS (Proc. Roy. Soc., 1928, **A**, **119**, 578—590).—The viscosity of neon has been determined over a range of temperature from 444·5° to −78·4° by means of a modification of the constant-volume method previously used by the author in the case of air (this vol., 116). The apparatus was specially designed for use with a gas available only in small quantities, and was calibrated in terms of a standard value for the viscosity of air. The standard chosen was that given by Millikan (Ann. Physik, 1913, [iv], **41**, 759), viz., $\eta_t=0·0001824-0·000000493(23-t)$ c.g.s. unit, over the range 23—12°, which gives $\eta_{15}=0·00017846$ c.g.s. unit. The values $\eta_{15}=3·076\times10^{-4}$ and $\eta_{100}=3·656\times10^{-4}$ were obtained for the viscosity of neon, which are in satisfactory agreement with Rankine's values (A., 1910, ii, 829). The theoretical formulæ of Lennard-Jones (cf. A., 1925, ii, 91) and Sutherland are discussed, and although the temperatures reached in the present investigation are not low enough to provide a crucial test between the two formulæ, it appears that Sutherland's formula is quite satisfactory for temperatures well above the liquefying point, but as that point is approached Lennard-Jones' formula becomes superior.

L. L. BIRCUMSHAW.

Internal friction of highly viscous substances. H. LEY and U. KIRCHNER (Z. anorg. Chem., 1928,

173, 395—410).—Closely concordant results for the viscosity of glycerol have been obtained by the transpiration method and by measuring the rate of fall of glass beads through a column of the liquid in a specially constructed apparatus. The mean value of η at 0° is 120·38 and at 20° 14·56 c.g.s. units.

In order to determine the effect of molecular configuration on the internal friction (viscosity) of liquids, the value of η for various stilbene derivatives has been determined at temperatures below the true m. p., *i.e.*, in the supercooled viscous state. In the homologous series of α-alkoxyphenylstilbenes the viscosity decreases logarithmically with rise of temperature and increases in the order: butoxy-, propoxy-, methoxy-, ethoxy-phenylstilbene, indicating that the side-chain of the higher homologues is oriented in the direction of the main groups and thus allows the molecules more readily to slide over one another. The introduction of a second methoxyl group into the molecule of the methoxy-compound to give α-(*p*-methoxyphenyl)-4-methoxystilbene causes a large increase in the viscosity owing to the enlargement of the molecule in two directions. This compound crystallises only with great difficulty and readily forms a thick syrup. The α-alkoxyphenylstilbenes are readily obtained by heating with concentrated formic acid the phenylbenzyl-*p*-alkoxyphenylcarbinol produced by treating magnesium benzyl chloride with the corresponding *p*-alkoxybenzophenone. The following derivatives of α-phenylstilbene are described: α-p-*methoxyphenylstilbene*, b. p. 240—242°/14 mm., d_4^{25} 1·1015, n_D^{25} 1·6660; α-p-*ethoxyphenylstilbene*, m. p. 76°, b. p. 242—244°/14 mm., d_4^{25} 1·0829, n_D^{25} 1·6536; α-p-*propoxyphenylstilbene*, m. p. 69°, b. p. 248—250°/14 mm., d_4^{25} 1·0676, n_D^{25} 1·6437; α-p-*butoxyphenylstilbene*, m. p. 82—83°, b. p. 259—260°/14 mm., d_4^{25} 1·0551, n_D^{25} 1·6333; α-p-*methoxyphenyl-4-methoxystilbene*, m. p. 64°, b. p. 260—262°/14 mm., d_4^{25} 1·1269, n_D^{25} 1·6641, α-Phenylstilbene has d_4^{25} 1·0719 and n_D^{25} 1·6678.

A. R. Powell.

Equal viscosities. II. W. Herz (Z. anorg. Chem., 1928, **173**, 411—412; cf. A., 1925, ii, 1049).—It is shown for 18 liquids that the ratio of the density at the temperature at which the viscosity is 0·0040 c.g.s. unit to the density at the critical temperature is approximately a constant. The recorded ratios vary from 2·739 to 2·967. A. R. Powell.

Magnetic double refraction of liquid mixtures. G. Szivessy and M. Richartz (Ann. Physik, 1928, [iv], **86**, 393—421).—The magnetic double refraction of 13 different binary liquid mixtures has been determined as a function of their volume concentrations. Excepting the mixtures of chloronaphthalene and cumene, the observed values do not agree with Langevin's theory, being generally lower than those demanded by the latter. J. W. Smith.

Composition of vapours from boiling binary solutions. D. F. Othmer (Ind. Eng. Chem., 1928, 20, 743—746).—A simple and rapid method for the determination of the composition of the liquid and vapour phases is described. The composition of the boiling liquid is maintained constant by returning the same amount of each constituent as is removed by vaporisation. Samples of the condensate and of the boiling liquid can be withdrawn separately for analysis. Vapour composition curves have been obtained for the following mixtures: water–acetic acid, benzene–acetic acid, hydrochloric acid–water, and acetone–methyl alcohol. The method is said to eliminate almost completely the errors inherent in the ordinary distillation methods.

The results suggest the existence of a second constant-b. p. mixture for the methyl alcohol–acetone series at about 94% (wt.) acetone, but definite proof of this is as yet wanting. R. A. Pratt.

Binary azeotropes. X. M. Lecat (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, i, 13—22).—A further list is given of the properties of mixtures, comprising 117 positive azeotropes (the b. p. of the azeotrope is lower than that of either component), four negative azeotropes, four eutectics, 57 non-azeotropic systems, and four systems where combination takes place. In each of the negative azeotropes a phenol is present. Acetamide is a constituent of the mixtures which show the greatest azeotropic lowering of b. p. It is pointed out that in mixtures of an ester of a mineral acid and an alcohol, double decomposition takes place, and the reaction proceeds in the direction of production of the more volatile ester. W. A. Richardson.

Azeotropy in the binary systems alcohols–hydrocarbons. M. Lecat (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, ii, 105—118).—Azeotropic data are given for the 344 systems formed by 29 alcohols and 39 hydrocarbons. Equations of the type $\delta=a-b\Delta+c\Delta^2-d\Delta^3$, where δ is the azeotropic lowering, Δ the difference in b. p. of constituents, and a, b, c, and d are constants, are given for the various alcohols studied. The value of δ decreases rapidly for an equal interval Δ as a series of monohydric alcohols is ascended. L. S. Theobald.

Azeotropy in binary alcohol–ester mixtures. M. Lecat (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, ii, 1—16).—The relation between the azeotropic lowering of b. p. and the difference in b. p. of the constituents for binary alcohol–ester mixtures is discussed. For systems containing methyl alcohol the relation is $\delta=9-0{\cdot}88\Delta+0{\cdot}033\Delta^2-0{\cdot}000485\Delta^3$, and similar expressions hold for other alcohols. The azeotropic lowering diminishes as the mol. wt. of the alcohol increases. Isomeric alcohols have the same δ/Δ relationship. Esters of mineral acids show greater azeotropic lowering than organic esters. Acetates give smaller lowering than formates and carbonates. Many of the systems show chemical reactivity, particularly at the b. p. W. A. Richardson.

Binary azeotropes. XI. M. Lecat (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, i, 54—62).—The data for 257 binary systems, azeotropic (positive), eutectic, and euzeotropic are tabulated. L. S. Theobald.

Sulphonitrous and sulphonitric [acid] mixtures. A. Sanfourche and L. Rondier (Compt. rend., 1928, **187**, 291—293).—The vapour pressure of mixtures of sulphuric acid with nitrous and/or nitric acids within the range of those which are met with in the chamber process increases with rise in temperature and with the nitrous or nitric acid content. For all mixtures of the three acids, particularly when the sulphuric acid is concentrated, the total pressure is higher than the sum of the individual pressures. The results for nitric acid may be explained by the reactions $HSO_4\cdot NO+HNO_3\rightleftharpoons H_2SO_4+N_2O_4$ and $2HSO_4\cdot NO+H_2O\rightleftharpoons 2H_2SO_4+N_2O_3$.

J. Grant.

Solubility of potassium bromide in acetone as related to the inter-ionic attraction theory. A. L. Robinson (J. Physical Chem., 1928, **32**, 1089—1093).—The solubility of potassium bromide in acetone, and in acetone solutions of sodium and potassium iodides and barium iodide and bromide has been determined at 25° up to an ionic strength of 0·004*M*. Large increases in solubility, of the magnitude required by the Debye–Hückel theory, were found.

L. S. Theobald.

Latent heat of fusion of naphthalene from new solubility data. A. A. Sunier and C. Rosenblum (J. Physical Chem., 1928, **32**, 1049—1055).—The solubility of naphthalene in ethylene chloride and bromide and in ethylidene chloride and bromide has been determined between 20° and 75°. The slopes of the curves connecting log. mol. fraction with $1/T$ (Abs.) support Ward's value of 970 (A., 1926, 1200) (except in the case of ethylene dichloride, which gives a slope of 960), indicating a value of 4440 g.-cal. for the molal latent heat of fusion of naphthalene.

L. S. Theobald.

Influence of structure on the solubilities of ethers. I. Aliphatic ethers. II. Cyclic ethers. G. M. Bennett and W. G. Philip (J.C.S., 1928, 1930—1937, 1937—1942).—The mutual solubilities of a number of ethers with water have been measured over the temperature range 0—25° by a modification of Hill's volumetric method (cf. A., 1923, ii, 467). The solubility of an ether in water increases with increased branching of the carbon chains of the alkyl groups, but in a homologous series the solubility falls rapidly as the carbon chain lengthens. Closure of a ring causes a large increase in the solubility; the smaller the ring the greater is the increase. The solubility of naphthalene in some of the ethers was found not to deviate seriously from the ideal solubility curves, indicating that, in the absence of water, the liquids are normal in behaviour. The considerable solubility of the ethers in water is attributed to their union with it to form a polar compound, and the results are discussed from this point of view.

J. W. Smith.

Theory of adsorption. T. Sexl (Z. Physik, 1928, **48**, 607—610).—The adsorption formula for a gas-solid interface deduced from statistical considerations is in agreement with the Langmuir formula.

J. W. Smith.

Absorption by colloidal oxides and active carbon of sulphur dioxide present in gaseous mixtures in small proportions. C. Ficai (Giorn. Chim. Ind. Appl., 1928, **10**, 199—203).—The absorption of sulphur dioxide by gelatinous silica containing 4·8% of water, hydrated alumina with 13·5% of water, and activated carbon is reversible and depends on the temperature. Active carbon absorbs more sulphur dioxide than the colloidal oxides and has the further advantage that its absorptive capacity is not sensibly diminished by the presence of water. Silica gel is, however, activated more readily and more cheaply.

T. H. Pope.

Volatility of nicotine. W. R. Harlan and R. M. Hixon (Ind. Eng. Chem., 1928, **20**, 723—724).—The volatility was determined at 25—40° by an air-bubbling method. The nicotine vapour was absorbed in 2*N*-sulphuric acid and determined by precipitation with silicotungstic acid. The vapour concentrations range from 1·76 mg. of nicotine per 10 litres of air at 25° to 6·04 mg. at 40°. The concentrations of nicotine in the vapour phase over hydrated lime dust and over " bentonite " dust are also recorded.

R. A. Pratt.

Adsorption by cadmium sulphide and its importance in the determination of cadmium. H. B. Weiser and E. J. Durham (J. Physical Chem., 1928, **32**, 1061—1064).—The chlorine adsorbed by cadmium sulphide precipitated from hydrochloric acid solutions of varying concentration by hydrogen sulphide at 25° and on cooling from 80° to 25° has been determined. Precipitation at 80° is incomplete. The amount of chlorine adsorbed depends on the acid concentration, the temperature, and the pressure at which precipitation is made. The phenomenon is one of adsorption and is not due to the formation of the salt $CdS,CdCl_2$ (cf. Treadwell, " Analytical Chemistry "). Continuous curves are obtained by plotting the amount of chlorine adsorbed against the concentration of hydrochloric acid for a fixed concentration of cadmium salt. The curve for 25° is a typical adsorption curve showing a maximum due to a change in the structure of the adsorbent. The curve obtained on cooling from 80° to 25° lies below that for 25° but is of a similar type; it shows, however, a minimum at an acid concentration 0·3*N*. The determination of cadmium as sulphide is of doubtful value, since it is questionable whether the conditions of precipitation can be maintained to give a product of known composition (cf. Egerton and Raleigh, J.C.S., 1923, **123**, 3019).

L. S. Theobald.

Adsorption of simple aliphatic compounds by cellulose. K. Brass and J. K. Frei (Kolloid-Z., 1928, **45**, 244—255).—The adsorption of aliphatic acids and other compounds by cotton wool and by precipitated cellulose (viscose) has been studied. All the acids examined, with the exception of palmitic and stearic acids, were adsorbed from aqueous solution. Formic and acetic acids, but not palmitic acid, were adsorbed by cellulose from solution in acetone. Formaldehyde, acetone, ethyl alcohol, glycol, and glycerol were not adsorbed from aqueous solution by cellulose. A few experiments conducted with aromatic compounds showed that the electrolytically dissociated acids were adsorbed and the undissociated phenols were dissolved. Benzoquinone was not adsorbed, thus resembling the aliphatic carbonyl compounds. No relation could be found between the mol. wt. of an acid and its degree of adsorption, but in most cases the acids with low dissociation constants were weakly adsorbed. Adsorbability appears to be a true function of the dissociation constant only when the acid is readily soluble.

Other investigators have found the adsorption of organic acids by filter-paper to depend mainly on the undissociated molecules, and it is suggested that the divergence of results is due to the structural differences between filter-paper and the cellulose used for these experiments. E. S. Hedges.

Adsorption of leuco-dyes by cellulose. K. Brass and G. Torinus (Kolloid-Z., 1928, **45**, 256—266).—The leuco-compounds of vat dyes are dissolved reversibly by cellulose, the order of magnitude of the partition coefficient between the vat solution and the cellulose differing widely (between 6 and 800) for different compounds. The partition coefficient appears to be related to the chemical constitution of the dye, for cyclic compounds, such as thioindigotin, and especially polycyclic systems, such as indanthrene and flavanthrene, have particularly high values. Leuco-dyes with high partition coefficients show great stability towards alkaline hyposulphite solution. The degree of dispersion of the leuco-compound does not appear to affect its solubility in cellulose. E. S. Hedges.

Influence of volume of solution and mass of adsorbent on the adsorption of arsenious acid by metallic hydroxides. K. C. Sen (Z. anorg. Chem., 1928, **174**, 75—81).—Isotherms for the adsorption by zirconium hydroxide of arsenious oxide sol have been determined under various conditions; for constant final concentration, reduction of the total volume of solution increases the extent of the adsorption, whilst increase of the total quantity of adsorbent present decreases the quantity adsorbed per unit weight of adsorbent, in addition, when the charge is considerable, to altering the curvature of the isotherms. Similar results are obtained when aluminium and chromium hydroxides are employed. It is assumed that this type of adsorption, which resembles that of cations by manganese dioxide, differs from adsorption by carbon, and is an example of chemical adsorption, in which the chemical affinity between the surfaces of the adsorbent and of the substance adsorbed plays an important part. H. F. Gillbe.

Influence of volume on the adsorption of arsenious acid by iron and aluminium hydroxides. K. C. Sen (Z anorg. Chem., 1928, **174**, 82—90).—Variation of the total volume of solution alters the adsorption isotherms and the adsorption constant. The quantity of manganese dioxide present in a solution of copper sulphate influences the isotherms of the adsorption process. H. F. Gillbe.

Equation of state for adsorbed phases. II. B. Tamamushi (Bull. Chem. Soc. Japan, 1928, **3**, 142—146; cf. Rideal, A., 1925, ii, 960).—The equation of state for the adsorbed phase is $P_s(A-\beta)=iRT$, where P_s is the lowering of surface tension, A the mol. surface of the adsorbent, β a correction term, and $1/i$ the lateral cohesion of the adsorbed molecules. The potential energy due to the latter is given by $U=-(\mu^2/r^3)f(\xi_d,e_0)$, where μ is the dipole moment, r the distance between the dipole centres, and $f(\xi_d,e_0)$ a function involving temperature and polarisation. The effect of temperature is evaluated by the Maxwell–Boltzmann principle and is $\bar{U}=\int Ue^{-U/KT}d\Omega/\int e^{-U/KT}d\Omega$, where U is the mean energy and Ω the solid angle. Finally, $1-i=(\mu/r^3)KT$, where $1-i$ is the ratio between electrostatic and kinetic energy. On calculating the dipole moment μ for normal butyric, valeric, hexoic, octoic, decoic, and dodecoic acids, a constant value of 20×10^{-19} e.s.u. is obtained; it follows that μ is characteristic only of the active carboxyl group when the molecules are not closely packed, when $\mu=30-90\times10^{-19}$. β is constant at 24—25×10^{-16} cm.^{2}/mol., corresponding with X-ray data for the cross-sectional area of the methyl group. For expanded films, β is greater. S. J. Gregg.

Measurement of interfacial tension of liquid–liquid systems. F. E. Bartell and F. L. Miller (J. Amer. Chem. Soc., 1928, **50**, 1961—1967).—Two simple forms of apparatus are described for the rapid and accurate determination of the interfacial tension between two liquids, which may be opaque. The apparatus is easy to construct and is readily cleaned. S. K. Tweedy.

Surface tension of some molten metals against molten salts. R. Lorenz and H. Adler (Z. anorg. Chem., 1928, **173**, 324—336).—The surface tension of molten cadmium chloride alone and admixed with potassium chloride has been determined in air at 600—750°. The value of k in the Eötvös–Ramsay–Shields formula for cadmium chloride from these results is 0·1653. The surface tension of molten cadmium against cadmium chloride at 725—730° is 3·9 dynes/cm. Addition of potassium chloride or of metallic lead causes a very rapid increase in this value and hence restrains the formation of a metal fog in the fused salt phase. A. R. Powell.

Unimolecular films. B. C. J. G. Knight and P. Stamberger (Nature, 1928, **122**, 97).—Experiments with films of vulcanised triolein and fatty acids indicate that in the polymerised products the molecules are joined side by side in a definitely oriented manner in long chains, leaving the polar groups unaltered. A. A. Eldridge.

Condensation of molecular streams on surfaces. J. D. Cockcroft (Proc. Roy. Soc., 1928, **A**, **119**, 293—312).—The phenomena previously studied by Wood (Phil. Mag., 1915, [vi], **30**, 300) and Knudsen (Ann. Physik, 1916, [iv], **50**, 472) have been investigated over a much wider range of temperature and by more accurate methods. In experiments with molecular streams, information is derived from the thickness of the deposit as to the intensity of the incident stream, and light is thrown on the nature and magnitude of the forces between the surface and the incident molecules. Three series of experiments were made: (1) an atomic stream of constant density was allowed to fall on a condensing surface in which a temperature gradient exists, and the region of deposition was observed; (2) an atomic stream was used of which the density varied from point to point of a condensing surface of constant temperature; (3) the effects of different surfaces and different surface conditions were studied. The first apparatus used was identical with that of Chariton and Seminoff (cf. A., 1924, ii, 723). The second apparatus consisted of a metallic oven which acts as a source of vapour for the issuing stream. The vapour issues from a hole in the end of a metal tube, so that its density has circular symmetry round the normal to the tube end surface, but decreases as the angle from the normal increases. The stream of varying density is allowed to fall on a condensing surface held at a constant and uniform temperature, ranging in different experiments from −70° to −160°. The results are considered from the point of view of Frenkel's adsorption theory (cf. A., 1925, ii, 194). On the basis of this theory, the method described enables the magnitude of the surface forces to be found for different adsorbed atoms and different surface materials. The true surface forces are in general masked by contaminating influences (probably gas films), so that to determine the magnitude of the real surface forces, special precautions must be taken to eliminate gas from the apparatus. It is probable that in the absence of gas films the critical temperature phenomena described by Wood and Knudsen (*loc. cit.*) would not exist for many surfaces. The experiments described show that, to ensure that practically all the atoms of the stream condense, it is sufficient to have the density of the stream about four times the critical density for the surface, but if liquid air temperatures are used for the condensing surface, the critical atomic stream density for cadmium may be so low as to require more than 10 hrs. for the first appearance of a deposit.

L. L. Bircumshaw.

Surface solutions. R. Delaplace (J. Phys. Radium, 1928, [vi], 9, 111—119).—An apparatus is described for measuring the pressure and area of surface solutions, and the pressure–area–temperature relations of surface solutions of benzoyl benzoate are examined at pressures of 0·1—0·001 dyne/cm., and at 15° and 27°. The laws of Boyle, pS=constant, and of Gay-Lussac, $pS=kT$, where p is the surface pressure, S the area of the surface, and k a constant, were verified. The value of k is much smaller than that of R, the gas constant. Attention is directed to the difference in experimental conditions between the author's work and that of Adam and Jessop (A., 1926, 348).

W. A. Richardson.

Surface activity of sodium salts of high-molecular fatty acids. P. Ekwall (Acta Acad. Åboensis Math. phys., 1927, 4, No. 6, 3—209; Chem. Zentr., 1928, i, 1156—1157).—The surface tension, conductivity, hydroxyl-ion concentration, colloid content, viscosity, and turbidity of aqueous solutions of sodium laurate, myristate, palmitate, and oleate were determined. The colloid content (acid salt) of all sodium laurate solutions less concentrated than 0·026*N* is low; in more concentrated solutions the quantity of neutral colloid rapidly increases. Between 0·008 and 0·026*N* the equivalent conductivity is practically independent of the concentration. Up to 0·026*N* the hydroxyl-ion concentration increases rapidly, and above 0·026*N* more rapidly. Below 0·006*N*, acid sodium laurate cannot exist. Sodium myristate solutions below 0·006*N* contain the acid salt, partly colloidal and partly as solid crystals. Above 0·005*N* the neutral colloid content rapidly increases and that of the crystallised acid soap diminishes. The hydroxyl-ion concentration increases in solutions up to 0·006*N*, and remains practically unchanged above this value. The equivalent conductivity is constant between 0·0015 and 0·005*N*. In sodium palmitate solution the specific conductivity is constant above 0·002*N*, and the hydroxyl-ion concentration above 0·0015*N*. Sodium oleate even in dilute solution is largely present in the colloidal condition. The relative colloid content, particularly that of the finely dispersed colloid, increases with concentration above 0·004*N*, whilst the hydroxyl-ion concentration, which has rapidly increased up to that point, becomes practically constant. Above 0·025*N* the equivalent conductivity is practically independent of concentration. Acid oleate cannot exist below 0·0009*N*. Near to the lower limit of existence the acid soap contains not more than 1 equivalent of acid to 1 equivalent of neutral soap, whilst in solutions containing larger quantities of the neutral colloid there is 1 equivalent of soap to 0·5 equivalent of fatty acid. The existence of colloid ions in sodium oleate solutions is postulated, and confirmed for concentrated solutions. McBain's ion-micelle theory is unnecessary in the case of saturated fatty acids. Soap solutions contain three kinds of surface-active substances: free fatty acid, acid soap, and undissociated soap molecules. The acid soap causes the greatest fall of surface tension. In certain cases capillary-active properties are exhibited by the three components in the colloidal form. The σ–c curves of the soap solutions are in complete accord with simultaneous structural changes. The surface tension falls rapidly with increasing soap content until the concentration above which acid soap can no longer exist is reached. It then remains practically constant until neutral colloid is present in large quantities, after which the surface activity falls again. In solutions containing so little soap that the acid soap is incapable of existence, the surface tension of the solution is determined essentially by the free fatty acid. The undissociated soap molecule aggregates also affect the value to a certain extent.

A. A. Eldridge.

Surface layer. VI. Differences of potential on the border between air and solutions of some benzene derivatives. A. Frumkin, A. Donde, and R. Kulvarski (Trans. Karpov Inst. Chem., 1926, No. 5, 17—33).—The fall of surface tension and the *P.D.* at the air–solution interface of solutions of aromatic compounds were studied. The adsorption of aromatic compounds is less than that of corresponding aliphatic compounds having the same number of carbon atoms. Introduction of a methyl group increases the adsorption, but the effect depends on its position. Compounds with one nuclear polar group (phenol, cresols, anisole, nitrobenzene, aniline, methylaniline, dimethylaniline, toluidines) communicate a positive charge to the surface of water, but the magnitude of the charge is less than for aliphatic compounds, and decreases with accumulation of polar groups; the charge becomes negative with dihydroxybenzenes, *m*- and *p*-nitrophenols. Compounds substituted in the side-chain (benzoic acid, methyl benzoate, benzyl alcohol, benzylamine) produce effects similar to those of corresponding aliphatic compounds. Compounds for which the molecules occupy in the surface layer less space than the corresponding isomeric compounds give more positive effects. Thus, *p*-cresol and *p*-toluidine give a more positive surface charge, whilst quinol and *p*-nitrophenol give a more negative surface charge, than the *ortho*-compounds. The difference is greater than can be ascribed to the change of degree of orientation of the molecules.

Chemical Abstracts.

Method of determining the absolute magnitude of surfaces. O. Hahn [with F. Bobek] (Annalen, 1928, **462**, 174—185).—An extension of previous work (A., 1925, ii, 177). The methods already described have been applied to the determination of the specific surfaces of two thorium salts, using uranium-*X* as the radioactive indicator. Thorium oxalate, precipitated from a hot solution of thorium nitrate by means of oxalic acid and then kept under the supernatant liquid for 2½ hrs. at 100°, had a specific surface (defined as g. of substance in surface per 1 g. of substance) of 0·0205%, whilst for thorium oxalate precipitated in the cold the corresponding figure was 0·136%. Thorium hypophosphate, obtained by precipitation of a boiling solution of the nitrate with sodium hypophosphate, gave the figure 9·35%. The absolute surfaces of the three specimens are therefore 0·12, 0·78, and 52 sq. cm., respectively, since the absolute surface$=p\sqrt[3]{N/Ms^2}$, where M=mol. wt., N is Loschmidt's number, p is the specific surface, and s is the density of the substance under examination. E. E. Turner.

Limiting surface effect in anisotropic liquids. W. Kast (Physikal. Z., 1928, **29**, 293—295).—Polemical. R. W. Lunt.

Prevalent error in the derivation of the f.-p. and b.-p. laws for dilute solutions. A. W. Davidson (J. Physical Chem., 1928, **32**, 1080—1085).—Theoretical. An error frequently made consists in writing $q_0=ml$, where q_0 is the heat evolved at T_0, the f. p. of the pure solvent. Since q_0 includes not only the heat evolved when the solvent freezes, but also that evolved during the removal of the solvent by osmotic work, it equals $ml+RT_0$. The familiar f.-p. expression should be corrected to $\Delta T/T_0=RT_0/(ml+RT_0)$ or RT_0/ml', where l' is the latent heat of fusion per g. at T, the f. p. of the solution. The usual b.-p. expression should be written $\Delta T/T=RT_0/ml_v'$, where l_v' is the latent heat of vaporisation at T, the b. p. of the solution. By a slight modification of the van 't Hoff cycle, the approximate form of the f.-p. equation for ideal solutions is derived in a simple manner. L. S. Theobald.

Cryoscopic irregularities with phenols. G. W. Richardson and P. W. Robertson (J.C.S., 1928, 1775—1783).—The variation with concentration of the f.-p. constant has been determined for a number of organic substances dissolved in phenol, *o*- and *p*-cresol. It is found that the equation $K=0{\cdot}02T^2/L$ does not hold even at low concentrations. Although the values of K at low concentration are of similar magnitude in most homologous series, increasing concentration tends to produce deviations in a direction characteristic of, but showing specific variation within, the series. These are supposed to depend on internal pressure and polarity in accordance with the theory of Hildebrand (A., 1916, ii, 518; 1919, ii, 392). This is supported by the relationship between changes in mol. volume on dissolution and cryoscopic behaviour. Derived phenols show markedly different magnitudes for K, although the deviations are similar, but this is not considered to be due to solid solution formation. Data are also given for the densities of various organic liquids at 40°. J. W. Smith.

Solutions of salts in pure acetic acid. I. A. W. Davidson (J. Amer. Chem. Soc., 1928, **50**, 1890—1895).—The following salts are practically insoluble in acetic acid: sulphates (sodium and ammonium sulphates are slightly soluble), silver halides, calcium carbonate, some sulphides. Double decomposition occurs in this solvent as readily as in water. Sulphates which normally form hydrates can be precipitated in the anhydrous state from acetic acid solution, even when the latter contains water. Except in the case of sodium carbonate solvolysis does not occur to any marked extent. Certain metal acetates behave in acetic acid like the corresponding bases in water, *e.g.*, zinc acetate is insoluble in the pure acid but dissolves readily when sodium acetate is added. S. K. Tweedy.

Osmotic pressures of concentrated solutions. J. H. Hildebrand (J. Physical Chem., 1928, **32**, 1086—1088).—Polemical against Bancroft and Davis (this vol., 239). L. S. Theobald.

Elevation in b. p. of saturated solutions at different atmospheric pressures. A. Mittenberg (Ukraine Chem. J., 1928, **3**, [Sci.], 119—123).—The elevation of b. p., ΔU_1, of saturated sodium chloride solutions at pressures of from 0·04—0·8 atm. is calculated from the formula $\Delta U_0/\Delta U_1=U_0^2C_0L_1/U_1^2C_1L_0$, where ΔU_0 is the elevation at 1 atm., U_0 and U_1 are the b. p. of the pure solvent at 1 atm. and at the given pressure, C_0 and C_1 the concentrations of salt, and L_0 and L_1 the corresponding latent heats of vaporisation. The calculated results are in satisfactory agreement with those found by experiment. R. Truszkowski.

Acid properties of concentrated solutions of zinc chloride. S. A. Vosnessenski and T. A. Stratonova (J. Russ. Phys. Chem. Soc., 1928, **60**, 771—782).—Zinc chloride forms acid complexes with water of the type $[ZnCl_2(OH)_n]H_n$ in concentrated solutions. The catalytic action of zinc chloride in those reactions which are catalysed by hydrogen ions is due to the formation of these complexes. This complex formation does not take place with the chlorides of lithium, potassium, calcium, manganese, magnesium, and cadmium. R. Truszkowski.

Constitution of magnesium acetate solutions. II. Evidence from vapour pressures. E. A. Goode, N. S. Bayliss, and A. C. D. Rivett (J.C.S., 1928, 1950—1955).—The vapour pressures of aqueous solutions of magnesium acetate up to a concentration of 4·55 g.-mol. per 1000 g. of water have been determined at 25° by a modified form of McBain and Salmon's dew-point method. The "molar fraction" calculated from the Raoult vapour-pressure formula passes through a maximum at a concentration of about 3·25 g.-mol. per 1000 g. This is explained in terms of the theory advanced by Rivett (A., 1926, 681) that in dilute solution the magnesium radical is hydrated, whilst in more concentrated solution molecular chain complexes are formed.

J. W. Smith.

Apparent hydration of ions. I. Densities and viscosities of saturated solutions of sodium and potassium chlorides in hydrochloric acid. J. W. Ingham (J.C.S., 1928, 1917—1930).—The solubilities of potassium and sodium chlorides in aqueous solutions of hydrochloric acid up to $13{\cdot}5N$ have been determined at 25° and the densities and viscosities of the saturated solutions measured. From the data obtained it is deduced that the chlorine ions are not hydrated and the potassium ions hydrated only to a slight extent. The hydrogen ions may be present in the form H_3O^+, but are probably not more highly hydrated. The viscosities of the solutions containing sodium chloride cannot be accounted for without a hydration factor of about 2, which decreases as the solution becomes more strongly acid. J. W. Smith.

State of some sparingly soluble hydroxides in solution in potassium hydroxide and ammonia solutions, as indicated by viscosity measurements. K. Mohanlal and N. R. Dhar (Z. anorg. Chem., 1928, **174**, 1—10).—The viscosity of N- and $0{\cdot}5N$-potassium hydroxide solutions is markedly increased by the presence of beryllium, aluminium, chromium, zinc, tin, and lead hydroxides, there being simultaneously a small decrease of the specific conductivity; there is a corresponding increase of the viscosity of ammoniacal solutions in presence of copper, cadmium, zinc, and silver hydroxides. Boric and benzoic acids cause a slight increase of the viscosity of potassium hydroxide solutions, whereas hydrogen chloride produces a decrease. The results obtained lead to the conclusion that the dissolved metallic hydroxides are present to some extent in the colloidal state. H. F. Gillbe.

Properties of colloidal lead. H. Q. Woodard (J. Amer. Chem. Soc., 1928, **50**, 1835—1840).—Lead sols prepared by the Bredig method are dark grey and fluorescent; they turn blue-black on keeping and appear brown by transmitted light. The particles are positively charged and on the passage of a current lead coagulates on the electrodes in arboriform growths. If protected by a layer of paraffin the sols are stable for 3—9 weeks, after which rapid coagulation sets in. The sols are readily coagulated by electrolytes, the coagulation time being roughly inversely proportional to the age of the sol. Shaking with air or carbon dioxide for a time which is shorter the greater the age of the sol also produces coagulation. The concentration of the colloid is proportional to the arcing current and to the p_H of the initial solution. With progressively increasing concentration of stabilising electrolyte (*e.g.*, potassium hydroxide) in the initial solution the lead concentration passes through a maximum. Contrary to the behaviour of gold, silver, and platinum sols, prolonged arcing does not diminish the maximum concentration.

S. K. Tweedy.

Aluminium hydroxide sol. K. J. Scheidt (J. Russ. Phys. Chem. Soc., 1928, **60**, 617—621).—When pure aluminium foil or wire is left in contact with clean mercury in distilled water for 12—24 hrs., a very sensitive sol of aluminium hydroxide possessing a high adsorptive power is formed. Traces of salts (except aluminium chloride) inhibit the formation, whilst hydrochloric acid stabilises it. By careful evaporation a concentration of 3·17 g./litre (in the presence of hydrochloric acid 4·5 g./litre) can be obtained. The sol is electropositive, the particles reaching a diameter of 340 μμ, and showing vigorous Brownian movement. The sol is easily precipitated by minute concentrations of ions, the hydroxyl and carbonate ions being especially effective. A theory of the mechanism of formation of the sol is discussed.

M. Zvegintzov.

Herapathite suspension. E. Hatschek (Kolloid-Z., 1928, **45**, 195—196).—Attempts have been made to prepare suspensions of herapathite, with the object of studying the optical properties of the sol in relation to those of the crystals of the disperse phase. The substance was prepared by precipitating a hot solution of quinine hydrogen sulphate in acetic acid with alcoholic iodine solution. Attempts to obtain a stable suspension by carrying out the reaction in very dilute solutions, and also by pouring the hot reaction mixture into a number of dispersion media (glycerol, tetrachloroethane, carbon tetrachloride, and benzyl alcohol), met with failure. No success was obtained when cellulose acetate was added to the dispersion medium as a protective colloid. The following method was successful: 4 g. of finely-powdered quinine sulphate are stirred energetically with 5 c.c. of 20% iodine in alcohol and 3 c.c. of glacial acetic acid until the colour of iodine has disappeared. A few drops of this mixture are added with constant agitation to a sol containing 1·5 g. of cellulose acetate in 100 c.c. of glacial acetic acid. A stable suspension with striking optical properties is produced, which is quite opaque in thick layers and when viewed by reflected light appears grey with a weak metallic shimmer. When stirred, the liquid shows bright metallic streaming zones, which disappear slowly in consequence of the high viscosity of the sol. A layer 7—8 mm. thick appears brown and turbid in transmitted light. The optical phenomena can be explained in terms of the optical properties of the crystals of herapathite.

E. S. Hedges.

Cerium hydroxide sols and gels. B. N. Desai (Kolloidchem. Beih., 1928, **26**, 422—438).—Sols prepared by dialysis of cerium ammonium nitrate in Bombay (25—27°) and in Edinburgh (17—19°) are compared. The time required for gel formation in the dialyser decreases considerably, and the degree of hydration of the gel increases, with rise in the temperature at which dialysis is carried out. Ultramicroscopical observation of the gel shows that it contains only amicrons. The fact that the refractive index is the same as that of water is explained as being due to the high degree of hydration of the gel. The manner in which water is combined in the cerium hydroxide particle is discussed, and a mechanism, based on the theory of residual valency, suggested. The results obtained on using the gel as an ultrafilter confirm Zsigmondy's assumption that the gel is capillary in structure, and its behaviour on cooling with a freezing mixture supports the view that it is polyphasic. The vapour-pressure isotherm was determined and found to be analogous to that of silica gel, except that there is no break in the cerium hydroxide curve. Viscosity measurements showed that the sol behaves as a highly hydrated colloid. On heating, the particles are dehydrated, and the viscosity–concentration curve of the heated sol is typical of a hydrophobic sol. L. L. Bircumshaw.

Behaviour of certain weak inorganic acids in solution. G. Jander (Z. angew. Chem., 1928, **41**, 201—203).—The behaviour of solutions of alkali tantalates, antimonates, and tungstates on acidification by dilute mineral acids, and the constitution of the gels which separate, have been studied by measurement of the diffusion coefficient at different hydrogen-ion concentrations and application of the equation $D_1\sqrt{M_1}=D_2\sqrt{M_2}$, where D_1 and D_2 and M_1 and M_2 are respectively the diffusion coefficients and the mol. wts. of the substance in solution at two different hydrogen-ion concentrations. The process has also been followed by the displacement of the limit of wave-length of light absorbed by the system. It is concluded that alkali tantalates contain the complex $M_7(Ta_5O_{16})$ and the gel precipitated by acids is composed of the acid $H_7(Ta_5O_{16})$. Antimonates and tungstates contain the simple ions SbO_3^- and WoO_3^-. The gel from antimonates is composed of $H_5Sb_3O_{16}$, whilst the precipitated tungstic acid may contain 5 to 12 atoms of tungsten.

W. A. Richardson.

Time of sedimentation of small particles in fluids. W. Weaver (Z. Physik, 1928, **49**, 311—314).—Polemical against Fürth (A., 1927, 1136).

R. W. Lunt.

Relation between hydration and stability of sols and the bivalent nature of the fluoride ion. S. Ghosh and N. R. Dhar (J. Indian Chem. Soc., 1928, **5**, 303—311).—Zirconium hydroxide sols have been prepared by dialysis of zirconium nitrate solution at the ordinary temperature and after boiling. The precipitation values of the chloride, bromide, and iodide ions are considerably greater for sols prepared by the first method, whilst those of the ferrocyanide, sulphate, oxalate, tartrate, and fluoride ions are but slightly greater. The sols are more readily coagulated when dilute, and the coagulation by a mixture of electrolytes is additive. The precipitation values of the sulphate, tartrate, oxalate, and fluoride ions are greater for chromium and aluminium hydroxide sols when prepared by the first method. These sols, and ferric hydroxide sols, are of lower viscosity than sols of zirconium and cerium hydroxides, and of vanadium pentoxide, whilst jellies are formed more readily by sols of the second group. High viscosity and tendency to jelly formation are ascribed to a high degree of solvation of the sol, which, however, appears not to be related to its stability. From its behaviour as a coagulating agent the fluoride ion is considered to be bivalent.

H. F. Gillbe.

Stability of disperse systems. E. N. Gapon (Ukraine Chem. J., 1928, **3**, [Sci.], 133—137).—The duration, Z, of a disperse system, the actual concentration, C, of the dispersed phase, and the degree of activity, S, of the continuous phase are related by $ZC=S$. The degree of dispersion of cupric chloride dihydrate, formed by passing dry hydrogen chloride through a solution of copper oleate in moist benzene, is uniform and the stability of this system diminishes with increasing water content. Where 12 molecules of hydrogen chloride are present to every molecule of copper oleate, the product ZC is constant, whence it follows that the activity of the medium is also constant. R. Truszkowski.

Action of α-particles on colloidal solutions of gold. J. E. Maisin (Ann. Soc. Sci. Bruxelles, 1928, B, **48**, 48—53).—The flocculation of a gold sol, containing 0·014 g./litre and prepared by the method of Zsigmondy, by the α-particles from radon has been followed by observations of the Tyndall effect in a specially-designed apparatus which is described. The curve obtained by plotting the relative lowering of the Tyndall effect against the quantity of radon used for coagulation rises somewhat to an arrest and then steeply, indicating a period of induction followed by coagulation proper. L. S. Theobald.

Dyeing of colloidal particles. A. Boutaric and F. Banès (Compt. rend., 1928, **187**, 117—119).—The adsorption of dyes by sols is less than that by the corresponding flocculated colloids. The particles of a sol behave like living cells in so far as the adsorption of colouring matter is concerned. Flocculated colloids behave like dead cells and fix all colouring matters. C. W. Gibby.

Reciprocal action of sols of ferric hydroxide, aluminium hydroxide, silicic acid, and manganese dioxide. I. W. N. Simakov (Kolloid-Z., 1928, **45**, 207—230).—The coagulation values of the sols used were determined with respect to univalent and bivalent anions and cations. The sols of manganese peroxide and silicic acid were found to be negatively charged, and the sols of ferric hydroxide and aluminium hydroxide carried a positive charge. A manganese dioxide sol is completely coagulated by ferric hydroxide sol when the ratio $MnO_2:Fe_2O_3=1:2{\cdot}222$ to $6{\cdot}097$, and by aluminium hydroxide sol when the ratio $MnO_2:Al_2O_3=1:0{\cdot}171$ to $0{\cdot}569$. Similarly, silicic acid sol is completely coagulated by a ferric hydroxide sol when the ratio $Fe_2O_3:SiO_2=1:1{\cdot}0$ to $1{\cdot}6$, and by aluminium hydroxide when the ratio $Al_2O_3:SiO_2=1:7{\cdot}204$ to $16{\cdot}007$. A mixture of two sols of equal sign is additive with respect to the amount of sol of opposite sign required to coagulate it. E. S. Hedges.

Ammonia test for unreduced gold compounds in red gold sols. P. P. von Weimarn (Kolloid-Z., 1928, **45**, 203—207).—The blue ring which often appears at the bounding surface of a concentrated ammonia solution and a red gold sol containing unreduced gold compounds is not produced by all gold compounds, and may not appear until after some time in other cases. Three groups of gold compounds can be distinguished in relation to this test: (*a*) those which give a blue ring in a short time, (*b*) those giving no blue ring, and (*c*) those which give a purple or blue ring after a long time. E. S. Hedges.

Influence of salts on the isoelectric behaviour of proteins. K. Kondo and T. Hayashi (Bull. Chem. Soc. Japan, 1928, 3, 146—151).—The isoelectric point of a protein is difficult to determine because the ions of the salt constituting the buffer solution may change both the mode and the extent of the ionisation of the protein molecule. Further, the salt may react with the protein, forming complex compounds which differ in solubility and ionisation from the original protein.

Experiments have been carried out on the flocculation of rice-glutelin by the addition of various inorganic chlorides. As the concentration of the salt increases, the precipitability of the protein at first diminishes, because the protein molecule is ionised and so dissolved, in proportion to the difference in "protein-ionising" powers between the anions and cations of the salt. Further increase in the salt concentration increases the precipitability, and finally diminishes it again, due to the formation of soluble dissociable complex compounds between the protein and the cations from the salt. Cupric, ferric, and aluminium salts give such compounds even at low concentrations, and this probably accounts for the poisoning effect of these salts on the soil.

S. J. Gregg.

Optical isomerides of cystine and their isoelectric solubilities. J. C. Andrews and E. J. de Beer (J. Physical Chem., 1928, 32, 1031—1039).—The solubility data obtained for isoelectric cystine in water at 25° for samples of different specific rotation indicate the existence of dextro-, lævo-, meso-, and racemic isomerides with the respective solubilities 0·32, 0·075, 0·088, and 0·152 g./litre.

L. S. Theobald.

Coagulation of thorium hydroxide sols by electrolytes. I. Kinetics of the coagulation. II. Relation between the purity of the sol and the influence of similarly charged ions on the electrolytic coagulation of thorium hydroxide sol. III. Stabilising action of alkali and alkaline-earth ions. IV. Coagulation by electrolyte mixtures. B. N. Desai (Kolloidchem. Beih., 1928, 26, 357—383, 384—404, 404—409, 410—421).—I. Details are given of a very accurate optical method, involving the use of a photo-electric vacuum cell, for measuring the coagulation velocity of thorium oxide. The ratio T_n/T is constant, as required by Smoluchowski's theory, only for a certain concentration of the coagulator. With increasing dilution the region of slow coagulation is reached, and the theory no longer holds. The results obtained are in approximate agreement with Freundlich's theory for slow and rapid coagulation. Reasons are given for the failure of previous investigators to observe the region of slow coagulation even when using dilute electrolytes, and the absence of a sigmoid curve with multivalent coagulating ions is explained by their high adsorbability. The values of the velocity coefficient K, calculated from the equation $dx/dt=K(1+bx)(1-x)$ (where $b=dx/dt$ at the turning-point of the x–t curve) are found to be fairly constant for each electrolyte, confirming the assumption that the coagulation is an autocatalytic process. On the other hand, different electrolytes give different K-values—*e.g.*, the values for potassium chloride are smaller than the corresponding values for lithium chloride. This is explained by the stronger stabilising action of the potassium as compared with the lithium ion. The values of p in the formulæ $T_n/T=(C/C_n)^p$ (Paine, *ibid.*, 1912, 4, 24) and $K/K_n=(C/C_n)^p$ (Freundlich) are found to vary with the dilution and with the electrolyte concentration taken as the normal value in calculating p.

II. In order to investigate the effect of dilution on the coagulation of thorium hydroxide sol by electrolytes, the phenomena observed on progressive dialysis were studied. Contrary to the requirements of the Schulze–Hardy law, the coagulation velocity curves for equivalent quantities of lithium, potassium, and barium chloride are not parallel for sols containing considerable quantities of a peptising agent. With increasing dialysis, the coagulation of the sol follows the Schulze–Hardy law more closely. The differences between the velocity curves are ascribed to the different adsorptions of similarly-charged ions by the sol. Deviations from the dilution rule are observed, but these diminish with rise in the concentration of the sol. The observed anomalies are most pronounced with univalent coagulating ions, but disappear with multivalent ions owing to the higher coagulating power and the greater adsorbability; the multivalent ions repress the adsorption of ions with the same charge as the sol. The assertion of Dhar (cf. A., 1924, ii, 737) that sols may be divided into two classes, according to whether they satisfy the dilution rule or not, is proved to be incorrect, since thorium hydroxide sol, according to the conditions chosen, may belong to either class.

III. The velocity of coagulation of thorium hydroxide sol by alkali and alkaline-earth chlorides has been measured. The Schulze–Hardy law does not hold in this case. The higher the valency of the ion carrying the same charge as the sol the greater is its peptising action. The ions, arranged in the order of their protective action, form the following series: $Li<Na\leq NH_4<K$, and $Mg<Ca<Sr<Ba$. The same order holds for the ionic mobilities.

IV. The coagulation velocity curves for the following pairs of electrolytes have been obtained: potassium and hydrogen chloride, potassium chloride and nitrate, potassium chloride and sulphate, potassium nitrate and sulphate, potassium nitrate and hydrogen chloride, hydrogen chloride and potassium sulphate, lithium and barium chloride. Ion antagonism is shown by the pairs potassium and hydrogen chloride, potassium nitrate and hydrogen chloride, potassium sulphate and hydrogen chloride, lithium and barium chloride. The antagonistic action is attributed to the adsorption of ions having the same charge as the sol, and Weiser's theory of the effect (cf. A., 1926, 242) is shown to have no experimental or theoretical support. Freundlich's view that ion antagonism is a characteristic of hydrophilic colloids is also shown to be incorrect. L. L. Bircumshaw.

Relations between coagulation, electrokinetic migration velocity, ion hydration, and chemical effect. Investigations on clay, quartz, and permutite suspensions. P. Tuorila (Kolloidchem. Beih., 1928, 27, 44—188).—Measurements of migration velocity have shown that the electro-endosmotic velocity of water at a glass surface is lowered by electrolytes in the following order : $LiCl < NaCl < KCl = KNO_3 < AgNO_3 = CsCl < HNO_3 < HCl$. The electrolytes retain the same order of effectiveness towards the lowering of the electrokinetic migration velocity of the particles of a paraffin sol and of a clay suspension, except for the silver ion, the position of which varies between $K = Ag$ and $Cs < Ag$, depending on the concentration of the silver nitrate. Counting the particles under the ultramicroscope has shown that Smoluchowski's formula holds for the slow coagulation of polydisperse paraffin sols, but not for clay suspensions. In the coagulation of a paraffin hydrosol, a clay suspension, a quartz suspension, and a suspension of sodium-permutite the order of influence of electrolytes is that given above, the position of the silver ion again being variable. There is thus a close relation between coagulation and electrokinetic migration velocity, which can be expressed in the case of paraffin particles by the formula $d\varepsilon/d\zeta = -k(\varepsilon)^p$. For both the coagulation and the lowering of migration velocity of the particles of suspensions of clay and of quartz, bivalent cations stand in the following order of influence : $MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$. The relation between coagulation and diminution of migration velocity can be expressed by a formula similar to that given for univalent cations. The formula of Smoluchowski is valid for the slow coagulation of clay suspensions by barium chloride. A suspension of sodium-permutite is peculiar, in that the order of cations given above holds for concentrated solutions, but is reversed for dilute solutions of electrolyte ; this is explained by the alkaline nature of the suspension. Suspensions of clay and sodium-permutite are stabilised by small amounts of sodium hydroxide towards coagulation by univalent cations, and a corresponding increase in migration velocity is observed. On the other hand, sodium hydroxide sensitises the suspensions towards coagulation by bivalent cations, the order of influence of the cations being reversed, according to whether the suspension is acid or alkaline. Simultaneously, the migration velocity increases, so that in this case there appears to be no relation between coagulation and migration velocity. The cause of this lies probably in the formation of colloidal hydroxides of the bivalent metals. Small amounts of sodium hydroxide sensitise the coagulation of quartz suspensions by both uni- and bi-valent cations. Experiments on the coagulation of systems, the anion of which forms an insoluble salt with the coagulating cation, showed that the coagulation may be (*a*) delayed (*e.g.*, the system copper sulphide–quartz suspension), (*b*) accelerated (copper hydroxide–clay suspension), or (*c*) unaltered (barium sulphate–sodium-permutite suspension). The chief influences are the sign of charge, the degree of dispersion, and the specific properties of the insoluble product. Systems with both positive and negative particles are readily coagulated. In a mixture containing positively-charged particles of copper hydroxide and negatively-charged particles of clay, the radius of effective sphere of action is about fifty times that of the colloidal particle.

E. S. HEDGES.

Inhibition by sugars of the precipitation of some metallic hydroxides from solution. K. C. SEN (Z. anorg. Chem., 1928, **174**, 61—74).—Sucrose aids the peptisation of zirconium, lanthanum, yttrium, and uranyl hydroxides; lactose and dextrose are effective only with the hydroxides of zirconium and uranyl, and lævulose with those of zirconium, uranium, and yttrium. In the case of lævulose and lanthanum hydroxide and lactose and yttrium hydroxide, peptisation occurs at first, but the solutions are unstable. The smaller the total volume of the solution and the greater the quantity of alkali present the smaller is the minimum quantity of sugar necessary for complete inhibition of precipitation. A certain excess of alkali is, however, necessary for peptisation to occur. The time factor is in many cases of importance, a cloudy solution often becoming clear when kept. Negative ions appear to have no influence.

H. F. GILLBE.

Acclimatisation and ionic antagonism with sheep serum and other colloids. S. PRAKASH, S. GHOSH, and N. R. DHAR (J. Indian Chem. Soc., 1928, **5**, 313—328).—Negative acclimatisation is produced in all cases when arsenious sulphide, mastic, and gamboge sols are coagulated by acids, and is greater for dilute than for concentrated sols; it is ascribed to the inhibition of hydrolysis. Dilute sheep serum is much more stable towards univalent ions than is the concentrated serum, whereas the reverse is true for multivalent cations and acids. Coagulation of serum by mixtures of cations having different valencies results in ionic antagonism. Coagulation by acids, and more especially by salts, produces positive acclimatisation; potassium fluoride and oxalate are exceptional, owing to the formation of the calcium salts. For salt coagulation, the acclimatisation is more evident in the dilute serum, the reverse being true for coagulation by acids. Ionic antagonism, positive acclimatisation, and the decrease of viscosity of sols when small amounts of electrolyte are introduced are due principally to the adsorption of similarly charged ions. The abnormal dilution effect of hydrolysable sols is due to increase of hydrolysis and of the ratio of the adsorptions of oppositely charged ions on dilution. Positive acclimatisation cannot be explained in terms of the theories of Freundlich, Bancroft, and Weiser, and is apparently connected with the ease of adsorption of the coagulating ions by the sol; it occurs only when the adsorption of ions with sign opposite to that of the sol is considerable, and the adsorption of the other ion is negligible.

H. F. GILLBE.

Swelling phenomena. Swelling of caoutchouc. P. STAMBERGER (Kolloid-Z., 1928, **45**, 239—244).—Experiments on the swelling of caoutchouc in toluene, benzene, and ethyl ether show that the caoutchouc gel is no longer in equilibrium when it is raised above the swelling medium. There is thus a difference between swelling in a liquid solvation medium and in the saturated vapour.

E. S. HEDGES.

Viscosity of agar and gelatin solutions in presence of alcohols and salts. A. JANEK and B. JIRGENSONS (Latvijas Farm. Zurn., 1927, No. 3, 9 pp.; Chem. Zentr., 1928, i, 1375).—Addition of an alcohol increases the viscosity of agar solution; addition of a salt reduces it whether alcohol is present or not. Gelatin behaves similarly, but the viscosity of alcoholic gelatin solution is lowered by potassium bromide, and raised by the sulphate or tartrate.

A. A. ELDRIDGE.

Dispersoidological investigations. XXII. Jellies and gelatinous precipitates, their classification, conditions of formation, structure, and industrial application. P. P. VON WEIMARN (Rep. Imp. Ind. Res. Inst. Osaka, 1928, 9, 1—196).—Jellies may be classified according to the degree of dispersion of their primary structural elements, giving four main groups—macrocrystalline, microcrystalline, ultramicrocrystalline, sub-ultramicrocrystalline—or according to their mechanical properties—resin-like jellies, paste-jellies, soft elastic jellies, solid jellies (glasses). The classification according to the concentration of the disperse phase is rejected as unsuitable, but a division into temperature-reversible and temperature-irreversible jellies is considered to be useful. The author distinguishes between network jellies, in which the whole mass sets uniformly, and coarse cellular jellies, in which gelation proceeds only on definite surfaces within the liquid. By thorough shaking of a coarse cellular jelly it is often possible to obtain a coherent network jelly, through breaking up of the membranes, although this is neither uniform nor transparent. The membranes of the cells of coarse cellular jellies are likened to plates cut from a network jelly of the same thickness.

The conditions necessary for the formation of network jellies, cellular jellies, and mixtures of the two are discussed and illustrated by an account of experiments on the production of jellies of the sulphates of calcium, strontium, and barium. Consideration is given to the state of the water in these jellies and it is believed that there is no fundamental difference between such preparations and typical jellies such as gelatin. The total amount of water imbibed by a jelly is supposed to consist of (1) interatomic hydration, *e.g.*, water in crystal hydrates ($Al_2O_3,3H_2O$; $SrSO_4,2H_2O$), (2) surface hydration, and (3) "structure" hydration, *i.e.*, water enclosed by the pores of the structural elements of the jelly. The production of colloidal solutions in an aqueous alcohol medium of barium, strontium, and calcium salts of the following acids: sulphuric, chromic, tungstic, molybdic, hydrofluoric, oxalic, tartaric, citric, carbonic, boric, orthophosphoric, arsenic, arsenious, hydrosulphuric, and silicic, and also of silver citrate, chloride, bromide, and iodide has been studied at low temperatures (to −30°), and the following conclusions have been reached. (1) Where only one type of salt can be formed (*e.g.*, barium sulphate, silver chloride) colloidal solutions are readily obtained, and excess of one component (barium ions for barium sulphate) gives a very stable colloid, whilst excess of the other component (sulphate ions for barium sulphate) diminishes the stability or causes coagulation. (2) Where more than one salt can be formed (*e.g.*, carbonates, phosphates, silicates, etc.), instead of stable colloidal solutions there are formed voluminous gelatinous precipitates, or, under suitable conditions, network jellies.

Photomicrographs of jellies of hydrated strontium sulphate are given, and these demonstrate that the tissue of the jelly is composed of bundles of thin needles; in each bundle, the needles spread radially from one centre, and the ends of the needles of different bundles are interwoven, forming a continuous structure. The following stages in the process can be observed: (1) formation of crystallisation centres, (2) development of these centres into spheres composed of needles, (3) union of the spherical bundles into flakes, (4) filling of the entire volume by the flakes, with complete soaking up of the mother solution. On keeping, the jellies disintegrate, with formation of a flocculent precipitate composed of aggregates of tangled needles. The needles are considered as primary structure elements of a jelly, and the spherical aggregates as secondary structure elements. The jellies are easily destroyed by energetic shaking, because the interlocking of the needles is disturbed. Examples are given of other jellies which are similarly destroyed by shaking. From the study of a number of photomicrographs of precipitated gold and of some other substances it is concluded that gelatinous precipitates are particular cases of flocculent precipitates; the individual grains of the former are ultramicro-crystals, the surface layers of which are strongly solvated, and the smaller the dimensions of the ultramicro-crystals and the greater the degree of solvation the more the precipitate assumes the properties of a jelly. There is no evidence that the ultimate particles of a jelly have of themselves a gelatinous nature.

Cellulose (filter-paper) can be spontaneously dispersed to give gelatinous spherulites by heating with a concentrated aqueous solution of calcium iodide. This process has been followed photomicrographically, and the forms produced resemble the spherulites of gelatin obtained by Bradford by slow evaporation of a gelatin sol; they also show a marked similarity to spherulitic aggregates of calcium arsenate prepared by the author. Theories of the structure of jellies and gelatinous precipitates are reviewed and criticised. It is considered that the unit of all jellies is at least sub-ultramicrocrystalline, and that no true emulsoid jellies, consisting entirely of liquid phases, exist. The examination of jellies and glasses by means of *X*-rays is discussed, and it is concluded that the individual structure elements are not devoid of an inner vectorial structure; absolutely amorphous jellies and glasses do not exist. It is stated as a general law that any substance can under suitable conditions be obtained as a stable jelly, and reference is made to the technical importance of this generalisation. E. S. HEDGES.

Viscosity changes at the beginning of the gelatinisation of dilute agar sols. H. G. B. DE JONG (Rec. trav. chim., 1928, 47, 797—818).—The viscosity of $\frac{1}{4}$% agar sols at 43° gradually increases to a value which remains constant for a short period and then increases again. The primary increase is quantitatively reproducible, whilst the second is completely irregular. It is suggested that the former corresponds with the formation of aggregates which are small compared with the cross-section of the capillary tube of the viscosimeter, the subsequent irregularity setting in when the size of the particles becomes so large as to exert a mechanical disturbance.

Electrolytes in very dilute solution exert a capillary electric action, whilst in greater concentration their influence becomes markedly lyotropic. The bearing of these results on the stability theory of Kruyt is discussed. F. J. WILKINS.

Electrokinetic potential of silicic acid gel. II. Effect of electrolytes. S. GLIXELLI and J. WIERTELAK (Kolloid-Z., 1928, **45**, 197—203; cf. A., 1927, 1139).—A study has been made of the influence of acids (nitric, hydrochloric, sulphuric, oxalic, and phosphoric) and salts (nitrates of potassium, barium, and lanthanum) at various concentrations, on the electrokinetic potential of silicic acid gel as measured by an electro-osmotic method. The discharging effect of the salts exhibits the usual connexion with the valency of the cation, but the hydrogen ion is unusually powerful, having a greater discharging effect than a tervalent cation. The relation of the electrokinetic potential to the concentration of inorganic salt solutions can be expressed by the formula $\zeta=a-K \log c$, where a and K are constants and c is the concentration of the solution. E. S. HEDGES.

Rule for the diffusion of electrolytes in charged gels. (MLLE.) CHOUCROUN (Compt. rend., 1928, **187**, 296—297; cf. this vol., 702).—The coefficients of diffusion at 28° of potassium ferrocyanide for neutral and alkaline gelatin are in the ratio 1 : 2·5, but are equal for neutral and alkaline water. The rate of diffusion of an electrolyte in a neutral gel is decreased when the sign of the charge on the latter is the same as that of the least mobile ion. J. GRANT.

Rhythmic phenomena in stones. Rhythmic conditions. M. STORZ (Kolloid-Z., 1928, **45**, 231—238).—Stones which are produced by the subsequent aggregation of the weathering products of rocks are described. Rhythmic banding, taking the form either of alternate zones of hardness or of colour, is often observed in these stones. This phenomenon is ascribed to a rhythmic change of external conditions during the formation of the stone. E. S. HEDGES.

Influence of electrolytes on the velocity of cataphoresis, and relation between the electrokinetic and electromotive potential, of gold. N. THON (Compt. rend., 1928, **187**, 119—122).—The effects of various electrolytes on the velocity of cataphoresis of aqueous gold sols and on the electrode potential of gold have been examined. The former effect, which may be either positive or negative, is due to the anions; the latter, which is negative, to the cations. C. W. GIBBY.

Ionisation accompanying the thermal decomposition of ozone. R. RUYSSEN (Natuurwetens. Tijds., 1928, **10**, 101—116)—The ionisation associated with the thermal decomposition of 10^{-6} to 10^{-7} mol. of ozone per sec. at 240° in a field of about 845 volts corresponds with a current of 10^{-11} to 10^{-12} amp. The ionisation increases directly with the rate of decomposition, and positive and negative ions are formed in equal numbers, and must thus have equal velocities. The ionisation increases rapidly with the intensity of the field, and has by no means reached its maximum in a field of 3000 volts per cm. The thermal decomposition of ozone thus occurs in two stages. The first is the breaking up of the molecule into positive and negative ions, and occurs with a measurable velocity dependent on the number of effective molecular collisions per sec.; the second, the combination of the ions to form oxygen molecules, appears to be instantaneous. S. I. LEVY.

Influence of intensive drying on the system nitrogen peroxide–nitric oxide–oxygen. J. W. SMITH (J.C.S., 1928, 1886—1894).—It is shown that when nitrogen peroxide is heated with phosphoric oxide at least three reactions occur simultaneously: (*a*) the reactants form an additive compound; (*b*) the peroxide is dissociated into nitric oxide and oxygen to a greater extent than in the moist gas, and these products do not recombine on cooling; (*c*) the nitric oxide decomposes into its elements at a greater rate than normally. The last effect is ascribed to the catalytic effect of the large surface of phosphoric oxide. The relative extent to which these reactions proceed depends on the temperature and duration of heating.

Nitrogen peroxide which has been intensively dried at the ordinary temperature does not dissociate very considerably into nitric oxide and oxygen when heated at 550° for 24 hrs., but when heated at 620° for the same time it seems to revert to the normal state, probably owing to a superficial decomposition of the glass. In the dried gas the rate of polymerisation of the coloured NO_2 molecules to form the colourless N_2O_4 molecules is retarded. J. W. SMITH.

Theory of electrolytic dissociation. W. NERNST (Z. physikal. Chem., 1928, **135**, 237—250).—See this vol., 127.

Theory of strong electrolytes. A. GYEMANT (Physikal. Z., 1928, **29**, 289—293).—Measurements have been made of the conductivity of 0·002 and 0·02N-solutions of hydrogen chloride in mixtures of ethyl alcohol and benzene containing 0·2% of water. The conductivity of the solution diminishes rapidly as the benzene content of the solvent is increased. In a magnetic field such solutions show an increase in conductivity in the direction of the field, but not transversely, the increase of conductivity being of the order of 1—2% per kilovolt cm.^{-1} If it be assumed that such solutions of strong electrolytes are not completely dissociated and if K denotes the dissociation constant of hydrogen chloride into ions, then the free energy of 1 g.-mol. of dissociated chloride is given by $-RT \log K$, which must also be equal to the electrical work of ionisation, A, less the work of dielectric solvatation, and the relationship takes the form $-RT \log K=A-\frac{1}{2}Ne^2(r_k^{-1}+r_a^{-1})(1-\varepsilon^{-1})$, where ε is the dielectric constant of the solvent and r_k and r_a denote the effective radius of cation and anion. It may be shown that for such very dilute solutions the molecular conductivity $\lambda=\lambda_\infty\sqrt{Kc_0}$, where λ_∞ denotes the molecular conductivity at infinite dilution and c_0 the total concentration of the electrolyte. From measurements of λ in a given solvent mixture (ε known) A may therefore be calculated, since the dielectric solvatation term can be calculated from known data. Using this value for A, K has been calculated as a function of c_0, *i.e.*, as a function of the composition of the solvent. These values of K have then been used to calculate λ, by the equation $\lambda=\lambda_\infty\sqrt{Kc_0}$, as a function of the composition of the solvent for the concentrations 0·002 and 0·02N of hydrogen chloride. Since the theoretical values thus calculated agree well with experimental values the data together with the Wien effect are thought to afford evidence for the incomplete dissociation of the electrolyte in such solutions.

R. W. Lunt.

Ionisation of hydrofluoric acid solutions. M. Auméras (J. Chim. phys., 1928, 25, 300—307).—It is shown that the conductivity of solutions of carefully purified hydrofluoric acid does not lead to a constant value of K in the equation $[H^+][F^-]=K[HF]$ (cf. Pick, Nernst Festschrift, 1912, 374). A chemical method (A., 1927, 312, 1141) leads to the value $16{\cdot}7\times10^{-5}$ for K, and it is shown that this method affords under certain conditions a means of determining the true degree of ionisation. W. A. Richardson.

Influence of neutral salts on acid–salt equilibria. III. Second dissociation constant of carbonic acid and influence of salts on the activity of hydrogen ions in a hydrogen carbonate–carbonate mixture. IV. Third and fourth dissociation constants of pyrophosphoric acid and influence of neutral salts on the activity of hydrogen ions in a ter–quadrivalent and di–tervalent pyrophosphate mixture, respectively. I. M. Kolthoff and W. Bosch (Rec. trav. chim., 1928, 47, 819—825, 826—833; cf. this vol., 589).—III. The second dissociation constant of carbonic acid has been determined by measurement of the p_{H} values of sodium carbonate–hydrogen carbonate mixtures at varying dilutions, and is given as $pK_2=10{\cdot}36$ at 18°. The Debye–Hückel equation holds for these solutions up to an ionic strength of 1·25. This equation, however, does not give a quantitative description of the behaviour of solutions containing an added neutral salt. There appears to be a specific interaction of ions which is dependent on the nature of the cation of the neutral salt and the size and valency of the ions in the acid–salt mixture.

IV. Similar measurements on solutions of sodium pyrophosphate and hydrochloric acid gave values of pK_3 6·679 and pK_4 9·391 at 18°. Whilst the neutral salt effect for a dilute mixture of bi- and ter-valent pyrophosphate can be calculated fairly accurately by means of the Debye–Hückel equation, it fails in the case of ter- and quadri-valent pyrophosphate solutions. F. J. Wilkins.

Dissociation constants of the naphthylaminesulphonic acids. I. M. Kolthoff (Chem. Weekblad, 1928, 25, 234).—The low values of these constants (Waterman and Groot, this vol., 407) are quite normal in the light of the "hybrid ion" conception of Bjerrum, *i.e.*, if they are regarded as the hydrolysis constants of the basic groups rather than the dissociation constants of the acid groups. The true dissociation constant of the amino-group, in the 2 : 5- and 2 : 8-acids, is calculated as about 10^{-10} and the isoelectric point as about $10^{-2\cdot5}$. S. I. Levy.

Absolute hydration of the hydrogen, lithium, sodium, potassium, chlorine, and bromine ions in normal solutions. J. Baborovský, J. Velišek, and A. Wagner (J. Chim. phys., 1928, 25, 452—481).—The true transport numbers of the cations and the electrolytic transference of water have been determined for solutions of hydrogen, lithium, sodium, and potassium chlorides, and lithium, sodium, and potassium bromides. The calculated values of the absolute hydration of the ions are, in mols. of water per ion : hydrogen 1·06, lithium 13—14, sodium 8—9, potassium 5, chlorine 4, and bromine 3.

H. F. Gillbe.

Conductivity and f.-p. measurements for the dimethylpyrone salts of acetic and the three chloroacetic acids in benzene solution. M. A. Rabinovitch (J. Russ. Phys. Chem. Soc., 1928, 60, 623—639).—The observations were intended to throw light on the electrolytic properties of the acids. The conductivities of 0·2N-benzene solutions of acetic acid in the presence of varying amounts of dimethylpyrone (up to a ratio of dimethylpyrone : acetic acid= 1·5) were determined, and found to give well-defined maxima. The conductivity of the free acids in benzene increases from trichloroacetic to acetic, but in the presence of dimethylpyrone this order is reversed, as in aqueous solutions. Cryoscopic determinations in benzene solution show that three salts are formed with dimethylpyrone : "acid" (dimethylpyrone) $(\text{acid})_2$; "neutral" (dimethylpyrone) (acid); and "basic" $(\text{dimethylpyrone})_2$ (acid). The stability of these salts increases from acetic to trichloroacetic, whereas the degree of polymerisation of the free acids decreases in that order. The maximum conductivity corresponds with the maximum concentration of the "acid" salt. The structure of these oxonium salts is discussed, and the nature of the ionisation in water, which is regarded as an "oxonium" base, is said to be due to complex formation. M. Zvegintzov.

Iodide, iodine, tri-iodide equilibrium and the free energy of formation of silver iodide. G. Jones and B. B. Kaplan (J. Amer. Chem. Soc., 1928, 50, 1845—1864).—The equilibrium constant, K, of the reaction $K^{\cdot}+I'+I_2=K^{\cdot}+I'_3$ was determined directly with the aid of the "equilibrator" (this vol., 863). The value of $K(=[I'][I_2]/[I_3'])$ shows no systematic variation with the concentration of iodine between the limits of 2—33% of saturation, nor with the concentration of the iodide between the limits 0·01—0·1N. At 0°, $K=0{\cdot}00072$, and at 25°, 0·00140; lower values are obtained when the solutions are saturated with iodine, especially when the iodide concentration is high, indicating the formation of higher polyiodides in the stronger solutions. By using a ballistic galvanometer and shunting a high-capacity condenser across it and its tapping key the measurement of potentials across a cell having an internal resistance of $1{\cdot}6\times10^6$ ohms to within 0·02 millivolt is possible; this enables cells of the Laurie type to be used. From the corrected *E.M.F.* of the cells $Pt|xN$-KI satd. with $I_2|xN$-KI unsatd. with $I_2|Pt$ (cf. Gerth, A., 1921, ii, 534), where x is 0·01—0·1, the unsaturated solutions being withdrawn from the equilibrator, the *E.M.F.* of the cell $Ag|AgI|I_2$ is calculated. The free energy of silver iodide ($Ag+\frac{1}{2}I_2=AgI$) is 15,802 g.-cal. at 25° and 15,680 g.-cal. at 0°; this is sensibly constant for concentrations of potass-

ium iodide between 0·01N and 0·05N. The entropy change is 4·8 g.-cal./1°, and the heat of formation at 25°, 14,354 g.-cal. All earlier work on the free energy of silver iodide is critically reviewed; it is shown that the value 2·19 g.-cal./1° for the entropy of silver iodide based on Nernst's specific heat measurements does not rest on a sound experimental basis.
S. K. Tweedy.

Changes in inter-atomic internal energy with reference to thermodynamics and catalytic action. R. D. Kleeman (Phil. Mag., 1928, [vii], **5**, 1191—1198).—The equation of state for a perfect gas should be written in the form $PV=M\xi RT$, where ξ is a function both of temperature and volume, whence it follows that the kinetic energy of a molecule is not exactly proportional to the temperature, but is also a function of the volume of the gas. It then follows that if substances which interact chemically are brought into contact with another substance, a change will take place in the inter-atomic energies of the reactants which will have the effect of either increasing or decreasing the rate of reaction. Thus a thermodynamic basis of the phenomenon of contact catalysis is offered.
A. E. Mitchell.

Thermodynamics of mixtures. V. Fischer (Z. Physik, 1928, **48**, 706—715; cf. this vol., 241).—An expression is deduced thermodynamically for the contraction of liquids on mixing. The heat of mixing, contraction, and vapour pressure for the sulphuric acid–water system are deduced and compared with experimental data.
J. W. Smith.

Thermodynamic relationships concerning the constitution of compounds of ter- and multivalent elements. G. Beck (Z. anorg. Chem., 1928, **174**, 31—41).—The densities and heats of dissolution of the sulphates and chlorides of ter- and quadrivalent metals in water and in alkaline solutions have been measured. The logarithmic contraction equation $kQ=546(\log V_a/V_c)$ (see A., 1927, 520) is discussed, especially in respect of the values assumed by the constant k for various groups of compounds.
H. F. Gillbe.

Second law of thermodynamics in chemistry. R. C. Cantelo (J. Physical Chem., 1928, **32**, 982—989).—Theoretical. From the chemical point of view the second law of thermodynamics is best expressed by the statement that "heat cannot be converted into work without compensation."
L. S. Theobald.

Energy of formation of the compound HCl,HBr. C. del Fresno (Anal. Fís. Quím., 1928, **26**, 164—167).—The heat of formation of the additive compound HCl,HBr has been calculated on the assumption that the structure is $H_2Br^+\cdot Cl^-$ and $H_2Cl^+\cdot Br^-$. The latter yields the higher figure, and is hence regarded as the more probable structure.
H. F. Gillbe.

Free energy of formation in fused salts. I. Copper and thallium halides, and mercuric iodide. G. Devoto (Gazzetta, 1928, **58**, 359—371; cf. Cambi and Devoto, this vol., 135).—The polarisation method, previously described, may be applied to the determination of the free energy of salts at their fusion points. The polarisation potentials at the fusion point were measured for the chloride, bromide, and iodide of univalent copper and thallium, and also for mercuric iodide. The potentials calculated fromf ree energy changes agree with the measured values to within about 0·05 volt.
F. G. Tryhorn.

Relationship between the different forms of calcium sulphate at high temperatures. P. N. Laschtschenko and D. J. Kompanski (J. Russ. Phys. Chem. Soc., 1928, **60**, 579—616).—The heating curves and densities of various hydrated modifications of calcium sulphate have been examined. The heating curve of native insoluble anhydrous calcium sulphate ("anhydrite") shows a break between 140° and 270°; previous to this the density reaches a maximum, due to an intramolecular change. Another break occurs between 958° and 984°, when the salt begins to dissociate. At 1190° there is a transition point from a rhombic to a monoclinic form. The hemihydrate, which is very difficult to obtain free from water, is stable up to 164°, when it begins to lose water and is gradually transformed into the anhydrous salt at 260°. "Soluble" anhydrous calcium sulphate (d 2·571) is prepared by prolonged drying of the precipitated dihydrate at 100° in a desiccator. A similar product is obtained by drying the metastable dihydrate obtained in the form of a gel. It readily absorbs water to give the hemihydrate. A break in the heating curve at 440—496° indicates transformation into the insoluble anhydrous salt. Above 165° and below 260° the hemihydrate may, depending on the conditions, be transformed into the "insoluble" or "soluble" (which is always the metastable phase) forms, or into a mixture of both. Gypsum, prepared by heating native or precipitated dihydrate at 500°, gives a cooling curve with breaks at 100—140°, 640—700°, and 975°. The first is due to the formation of the unstable monohydrate, followed by polymerisation to the hemihydrate, the second corresponds with the temperature at which dead-burnt gypsum recovers the power to "set" with water, whilst the third is the point of dissociation.

The possible structural formulæ of the various modifications and the processes involved in the "setting" of plaster of Paris are discussed.
M. Zvegintzov.

Tin–antimony alloys. W. Bronievski and L. Slivovski (Rev. Mét., 1928, **25**, 312—321).—A more detailed account of work already published (this vol., 829).

Gold–platinum alloys. A. G. Grigoriev (Ann. Inst. Platine, 1928, **6**, 184—194).—A fusion diagram is constructed for mixtures of gold and platinum. No compound formation occurs, but solid solutions are formed. The micro-structure of the alloys formed is of the ordinary type in such cases. The hardness of the alloys rises to a maximum at about 70% Pt.
R. Truszkowski.

Transformations of the β-phase in the copper–zinc system. P. Saldau and J. Schmidt (Z. anorg. Chem., 1928, **173**, 273—286).—The boundaries of the β-phase in copper–zinc alloys have been determined by tempering at various temperatures for 84 days followed by quenching and examination of the microstructure. Below 600° no decomposition into $\alpha+\gamma$ was observed. Below 440° the limiting composition of β is 55·01—51·39 at.-% Cu in cast alloys and 54·63—49 at.-% Cu in tempered alloys. At 480° the field of pure β in tempered alloys extends from 56·01 at.-% Cu to 51·39 at.-% Cu; above 480° the field broadens on both sides. In the temperature interval 440—480° a discontinuity occurs in the equilibrium diagram indicating the existence of two modifications of β, viz., β', stable below 440°, and β, stable only above 480°. The discrepancies found by previous workers in the limiting compositions of the β-field are ascribed to insufficient time of annealing to obtain complete equilibrium being used in their work. A. R. Powell.

Dissociation of chromium nitride. G. Valensi (Compt. rend., 1928, **187**, 293—296).—The dissociation isotherms between 810° and 1200° of chromium nitride, prepared by heating pyrophoric chromium in pure nitrogen at 800°, are analogous to those of palladium and hydrogen, and indicate the formation of the compound CrN. The temperature (1015°) at which the dissociation pressure is 760 mm. agrees with the calculated value. J. Grant.

Physico-chemical investigations on the higher fatty acids. I. Thermal analysis of fatty acids. A. Binary systems tristearin–tripalmitin and stearic acid–palmitic acid. N. N. Efremov (Ann. Inst. Polyt. Ural, 1927, **6**, 155—202).—The data given in the literature for the equilibrium in the system stearic–palmitic acids are inaccurate (cf. de Visser, A., 1898, i, 560; 1899, i, 255; Carlinfanti and Levi-Malvano, A., 1910, i, 5). The temperature–concentration diagram corresponds with Roozeboom's type III, showing the formation of two series of solid solutions and passing from one to the other through a minimum at 52·5° (68% by weight of palmitic acid) without interruption of the continuity. From the fused mixtures no chemical compound is formed on cooling. The solid solutions decompose extremely slowly, yielding either a chemical compound of varying composition of the Berthelot type or a mechanical mixture of the components with a eutectic point. The diagram of the pressure of flow (Kurnakov and others, A., 1911, ii, 18; Z. anorg. Chem., 1911, **76**, 241) for this system, which confirms the results of thermal analysis, consists of a continuous curve with a high maximum corresponding with 45% by weight of palmitic acid and the pressure 10·55 kg./mm.^{2} The pressure of flow of the solid solutions falls considerably after 2 months, owing to the decomposition of these solutions; thus the maximum pressure is reduced to 7·5 kg. per sq. mm., the corresponding composition remaining as before. Determination of the viscosity furnishes an excellent means of ascertaining the degree of purity of stearic and palmitic acids. The micro-structure is that characteristic of continuous solid solutions, no new phases indicative of the formation of a chemical compound being observed; the micro-structure also reveals incipient decomposition of the solid solutions after these have been kept for 2 months.

Both tristearin and tripalmitin exist in not less than three polymorphous modifications. The stable α-forms are obtained on rapid cooling of the molten glycerides to the solidifying temperatures (53·2° and 48·4°, respectively), and are converted into the soft, transparent, labile β-modifications if kept at 53·2—55·2° and 48·4—53·8°, respectively. When carefully heated, these do not melt, but lose their softness and transparency and change into the γ-forms. The temperature–concentration diagram of the system tristearin–tripalmitin represents one of the most perfect examples of isomorphism of the components. Continuous solid solutions are formed by the α-modifications, the curve showing a minimum at 44·9° (79·5% tripalmitin). The β-forms give a similar curve with a minimum at 47·8° for 75% of tripalmitin. A third curve is given which corresponds with the conversion of the β- into the γ-modifications, the minimum being at 52·3° (72·4% tripalmitin); all the intermediate mixtures exhibit similar relationships. On the other hand, the m. p. of the γ-forms of tristearin (69·3°) and tripalmitin (67·5°) rapidly fall in mixtures, so that the curve gradually approaches the preceding curve.

Measurement of the m. p. of fats and fatty acids by means of Schukov's apparatus and a thermometer yields only approximate figures and is useful mainly owing to its simplicity and rapidity. Prevention of supercooling by seeding and stirring leads to values more nearly in agreement with those obtained by means of a thermo-element in conjunction with a pyrometer. With these poorly crystallising substances, replacement of the cooling curves by heating curves results, even under the favourable conditions, in high values for the m. p. When these substances are heated in a capillary, the m. p. is inevitably raised and the solidifying point lowered, and differences as great as 10° between these temperatures are obtainable. T. H. Pope.

Pseudo-ternary systems containing sulphur. III. System sulphur–sulphur monochloride. D. L. Hammick and M. Zvegintzov (J.C.S., 1928, 1785—1791).—The solubility of sulphur in sulphur monochloride has been determined both with and without previous heating of the solution to a definite higher temperature. In confirmation of the observations of Aten (A., 1913, ii, 40) it is found that the solubility is greater the higher the temperature to which the solution has been preheated. The solubility curves are said to indicate that the phenomenon is due to the formation of a subchloride S_4Cl_2 and not to a change in the inner equilibrium of the dissolved sulphur. J. W. Smith.

System $KCl–HCl–H_2O$ between 0° and 80°. G. Malquori (Atti R. Accad. Lincei, 1928, [vi], 7, 738—739).—To supplement the results obtained at 25° (A., 1927, 628) the solubility of potassium chloride in hydrochloric acid solutions has been determined at 40°, 60°, and 80°. The solubility decreases with increasing acid content, but the shape of the curves does not alter with the temperature. O. J. Walker.

System $AlCl_3–HCl–H_2O$ between 0° and 80°. G. Malquori (Atti R. Accad. Lincei, 1928, [vi], 7, 740—744).—From the f.-p. and solubility curves of the system $AlCl_3–H_2O$ it is shown that between the cryohydric temperature (—55°) and 80° the saturated solution is in equilibrium with the hydrate $AlCl_3,6H_2O$ as solid phase. The heat of dissolution of this hydrate at 20° is 4606 g.-cal. The solubility of aluminium chloride in presence of hydrochloric acid was determined at 0°, 40°, 60°, and 80°. The acid decreases the solubility of the salt, but the temperature does not affect the shape of the curves. O. J. WALKER.

System $AlCl_3$–KCl–H_2O between 0° and 80°. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 745—747; cf. preceding abstract).—The solubility of aluminium chloride in presence of potassium chloride has been measured at the same temperatures. Similar results are obtained. O. J. WALKER.

Systems $Pb(NO_3)_2$–$LiNO_3$–H_2O and $Pb(NO_3)_2$–$CsNO_3$–H_2O. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 495—496).—A preliminary note in which the equilibrium solutions at 25° are presented in the form of a triangular diagram. R. W. LUNT.

Formation of double sulphate of cerium and rubidium. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1928, [vi], **7**, 449—452).—From an examination of the system $Ce_2(SO_4)_3$–Rb_2SO_4–H_2O at 25° it is concluded that the only double salt formed has the composition $Ca(SO_4)_3,Rb_2SO_4,2H_2O$. Crystallographic data for this substance are given.

R. W. LUNT.

System Na_2CO_3–$NaHCO_3$–H_2O and the range of existence of "trona." R. WEGSCHEIDER and J. MEHL (Monatsh., 1928, **49**, 283—315; cf. Hill and Bacon, A., 1927, 1142).—A study of the equilibrium has been made at eleven temperatures between 20° and 94·5° and at 30·0°, 49·7°, and 89·5° in presence of sodium chloride. The range of existence of the double salt "trona," $NaHCO_3,Na_2CO_3,H_2O$, has been deduced from the results. One or possibly two double salts appear at 90° which have a higher carbon dioxide content than "trona." The latter yields a *labile* (β) *sodium hydrogen carbonate* when treated with water. I. VOGEL.

Equilibria in the ternary system chromium trioxide–sulphur trioxide–water. A. W. RAKOVSKI and D. N. TARASSENKOV (Z. anorg. Chem., 1928, **174**, 91—96).—The solubility curves of chromium trioxide in aqueous sulphuric acid solutions have been determined at 0°, 20°, 40°, 75°, and 100°. The curves may be followed for a considerable distance into the metastable region which is entered after a minimum at 57·76% of sulphur trioxide in the liquid phase. The compound CrO_3,SO_3 exists and may be employed as an indication of moisture in closed systems, since at the ordinary temperature it decomposes with a marked change of colour if the relative humidity exceeds 1·7%. The hydrate $SO_3,2H_2O$ forms metastable mixed crystals with chromium trioxide.

H. F. GILLBE.

Reduction of metallic oxides; equilibrium $Zn+CO_2 \rightleftharpoons ZnO+CO$. K. JELLINEK and B. POTIECHIN (Z. anorg. Chem., 1928, **173**, 164—168).—The reaction $Zn+CO_2 \rightleftharpoons ZnO+CO$ has been studied at 565°; the quantity of carbon dioxide present at equilibrium is about 0·2%. The discrepancy between this value and that obtained by other observers is ascribed to differences in the form of the zinc oxide employed. H. F. GILLBE.

System cupric sulphate–ammonium oxalate–ammonia. M. HERSCHKOVITSCH (Z. anorg. Chem., 1928, **173**, 222—224).—A 0·04M-solution of cupric sulphate with four times the quantity of ammonium oxalate yields an electrolyte from which a brilliant, dense, and adherent copper deposit may be obtained. The muddy deposit which is liable to form in the bath is due to excess of either ammonia or oxalic acid. In presence of an excess of ammonia the deposit consists of a mixture of crystals of the composition $Cu(CO_2)_2,NH_3$, $Cu(CO_2)_2,2NH_3$, and $Cu(CO_2)_2,2NH_3,2H_2O$, whilst if oxalic acid be present in excess, the deposit is cupric oxalate.

H. F. GILLBE.

Thermochemistry of fluorine. H. VON WARTENBERG (Z. anorg. Chem., 1928, **174**, 96; cf. A., 1926, 476).—The final equation should read $Cr+3/2F_2+aq.=CrF_3,aq.+283{\cdot}3+a$. H. F. GILLBE.

Source of error in conductivity measurements. L. DE BROUCKÈRE (J. Chim. phys., 1928, **25**, 294—299).—The conductivity of 0·01N-solutions of various chlorides in a vessel with freshly-platinised electrodes has been measured, and it is shown that the conductivity decreases, reaching an equilibrium value, some tenths of 1% lower than the original value, in about 12 hrs. If the solution is now replaced the conductivity rises nearly to the initial value in the first experiment, and remains very nearly constant. If the same electrodes are used for measurements in 0·001N-solutions a gradual increase in conductivity is observed. When the electrodes are removed from the 0·01N-solutions chloride can be washed out by immersion in pure water, and the amount thus obtained is equal to the amount lost from the original solution. The amount of salt adsorbed varies with each replatinisation. W. A. RICHARDSON.

Electrical conductivity of aqueous solutions of radon. E. GLEDITSCH and L. GLEDITSCH (J. Chim. phys., 1928, **25**, 290—293).—Conductivity measurements on solutions containing quantities of radon varying from 13·5 to 235×10^{-9} curie per c.c. in presence or in absence of electrolytes show that the niton has no influence on the conductivity of the solutions. W. A. RICHARDSON.

Conductivity and viscosity of solutions of lithium nitrate in certain mixed solvents [at 25°]. J. L. WHITMAN and S. R. SPENCER (J. Amer. Chem. Soc., 1928, **50**, 1840—1844).—Water, methyl and ethyl alcohols, and mixtures of these were used as solvents, the viscosities being measured in an Ostwald viscosimeter. The results are compared with those of Jones (A., 1905, ii, 73). The values recorded are uniformly higher than those of Jones, possibly because of the difficulty of drying lithium nitrate, which can be completely dehydrated only by prolonged heating at 150° in a vacuum. S. K. TWEEDY.

Dispersion of conductivity and dielectric constant for strong electrolytes. P. DEBYE and H. FALKENHAGEN (Physikal. Z., 1928, **29**, 401—426).—The theory previously developed (this vol., 596) has been extended by taking into account the Brownian motion of the ions and the cataphoretic action. In this manner laws of a more quantitative nature are deduced. The theoretical values deduced are compared with experimental data. J. W. SMITH.

Electrochemistry of the system benzamide–bromine–nitrobenzene. V. C. Finkelstein and O. K. Kudra (J. Russ. Phys. Chem. Soc., 1928, **60**, 783—793).—The conductivity at 25° and 35° of nitrobenzene solutions containing bromine and benzamide in proportions corresponding with the compound NH_2Bz,Br_2 increases continuously with the concentration, up to 52%. The molecular conductivity curves at 35° show a maximum at $v=0{\cdot}9$ litre. The presence of bromine in excess increases the conductivity. On electrolysis, bromine is evolved at the anode and benzamide is deposited on the cathode.

R. Truszkowski.

Revision of the theory of transfer resistance. E. Newbery (Proc. Roy. Soc., 1928, A, **119**, 686—689).—A number of experiments have been made with a new type of electrolytic cell, designed to eliminate the disturbing effect of the fall of potential through the electrolyte obtained with the type of cell used in previous work. The table showing the relation between transfer resistance and the concentration of the electrolyte, previously recorded (*ibid.*, 1926, A, **111**, 188), is found to be incorrect. It is now found that transfer resistance occurs only when a gas is being liberated at an electrode. It is independent of the concentration of the electrolyte and increases with rise of temperature. The highest values are obtained with very low current densities; at high current densities, transfer resistances become very small. The theory of the effect is discussed. It is suggested that transfer resistance is the electrical resistance of a film of gas over the electrode surface.

L. L. Bircumshaw.

Apparatus for the moving boundary method of determining transference numbers. E. R. Smith (J. Amer. Chem. Soc., 1928, **50**, 1904—1906).—An apparatus is described which obviates the necessity of calibrating the measuring tube. One side of the apparatus is closed and is connected with a tube of mercury; mercury is withdrawn so as to oppose the motion of the boundary, the weight withdrawn giving the volume through which the boundary has moved. The boundary can repeatedly be returned to the starting point for a fresh determination.

S. K. Tweedy.

Measuring *P.D.* by means of dropping electrodes. A. Frumkin and A. Donde (Trans. Karpov Inst. Chem., 1926, No. 5, 34—38).—If the water electrode in Kendrick's apparatus is replaced by a mercury dropping electrode, the *P.D.* at the air–solution boundary can be measured.

Chemical Abstracts.

Influence of pressure on the potential of electrodes charged with hydrogen and on the current–potential curves. G. Tammann and E. Jenckel (Z. anorg. Chem., 1928, **173**, 337—357).—In the cell $(Pd)H_2|2N\text{-}H_2SO_4|CdSO_4|Cd$ the value of $\Delta E/p$ decreases slightly with increasing pressure, the rate of decrease being the smaller the higher is the temperature. Similar results are obtained with the cell $(Pt)H_2|0{\cdot}1N\text{-}HCl|CdCl_2|Cd$. The effect of pressure on the potential of platinum electrodes in oxidising and reducing solutions has been measured; the curves are in all cases approximately straight lines. In ferrous and ferric chloride solutions, pyrogallol, and quinhydrone the potential becomes less noble with increase of pressure and in potassium ferro- and ferri-cyanide solutions more noble. The potential of the quinhydrone electrode becomes more positive with addition of neutral salts, lithium chloride having the most pronounced effect; this effect, however, is relatively small. The potential of palladium feebly charged with hydrogen becomes more noble on keeping owing to diffusion of the surface hydrogen into the body of the metal. The effect of pressure on the current–*E.M.F.* curves of the cells $Ni|KOH|Ni$, $Hg|H_2SO_4|Pt$, $Pb|KOH|Pt$, $Pb|H_2SO_4|Pt$, and $Pt|ZnSO_4|Pt$ is shown in a series of curves; in all cases increase of pressure gives a higher *E.M.F.* for the same current.

A. R. Powell.

Electrode potential of single crystals of iron. K. Iwasé and K. Miyazaki (Sci. Rep. Tôhoku Imp. Univ., 1928, **17**, 163—167).—The electrode potential of the (110) face of an iron single crystal was found to be much greater than that of polycrystalline iron. With the latter the *E.M.F.* rises to a maximum and then falls, due to dissolution of the iron and contamination of the surface, whilst with the single crystal a constant value is attained representing the true *E.M.F.* between iron and the solution.

C. J. Smithells.

Change of the potential of metals, and of the colour and resistance of certain gold–silver–copper alloys, on cold rolling. G. Tammann and C. Wilson (Z. anorg. Chem., 1928, **173**, 156—163).—The surfaces of copper, silver, lead, zinc, cadmium, and molybdenum plates become less noble when polished; the effect is reversed on heating. Certain alloys of gold, silver, and copper become noticeably yellower on rolling, but on heating the colour commences to fade from about 200° upwards. At this temperature the electrical resistance also commences to decrease to a minimum, as is the case with the components. The latter, however, then show an increase of resistance until the neighbourhood of the m. p. is attained, whereas the alloys exhibit further smaller minima, which run parallel with changes in the colour of the alloys.

H. F. Gillbe.

Electrolytic reduction potentials of organic compounds. III. Nicotinic acid. M. Shikata and I. Tachi (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 95—96; cf. this vol., 648).—The first stage of the reduction of nicotinic acid consists in the reduction of the carbonyl to the formyl group, and the second stage is the reduction of the pyridine ring. Reduction does not take place in excess of alkali.

Chemical Abstracts.

Mechanism of oxidation–reduction potential. I. Oxidation–reduction potential of cysteine and cystine. E. C. Kendall and D. F. Loewen (Biochem. J., 1928, **22**, 669—682).—Dixon's hypothesis (A., 1927, 209) of a "steady state" depending on a kinetic equilibrium between the dissociation of hydrogen from cysteine and diffusion of hydrogen from the surface of the metal electrode is not supported by experimental evidence. The drift in the reduction potential with a platinum electrode is due to traces of oxygen or other oxidising agents adsorbed on the surface of the metal. The steady potential given by a gold electrode is due to the failure of the gold to adsorb oxygen. The higher reduction potential with the mercury electrode is shown to be due to the failure of the oxidant to affect the mercury to the same extent as it does platinum and gold. The difference in potential between the gold and mercury electrodes in a solution of cysteine cannot be explained by the higher overvoltage of hydrogen on mercury.

Cysteine on oxidation does not form cystine immediately. An intermediate product which acts as the oxidant is formed. This product exists in a low concentration. In the absence of an activating agent cystine does not affect the platinum electrode and the reduction potential is a function of the logarithm of the concentration of cysteine. In a solution of cysteine and cystine containing an activating agent, cystine is brought into equilibrium with the oxidant and the reduction potential is determined by the ratio C·SH : C·S·S·C groups. S. S. ZILVA.

Reduction potential of cysteine. D. C. HARRISON and J. H. QUASTEL (Biochem. J., 1928, 22, 683—688).—Metal-free cysteine gives at a gold electrode a high negative reduction potential which is not increased by the addition of traces of catalysts such as ferric or cupric ions. This is contrary to the result which would be expected on Dixon's hypothesis (A., 1927, 209) of the mechanism by which the reduction potential of cysteine is secured at the electrode. S. S. ZILVA.

Photochemical cell containing potassium ferrocyanide solution. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, Suppl., 11—13).—A cell containing potassium ferrocyanide solution and having platinum electrodes in the two compartments, which are separated, although not completely, by a porcelain diaphragm, yields at a time t after commencement of illumination of one of the compartments a *P.D.* $\pi=\lambda(1-e^{-0\cdot 8kt})$, whilst on discontinuing the illumination $\pi=\lambda(1-\gamma t)/(1+\delta\sqrt{t})$, where λ is the equilibrium potential, and γ, δ, and k are constants. The *E.M.F.* is due to displacement to the right of the equilibrium $[Fe(CN)_6]'''' + 2H_2O \rightleftharpoons [Fe(CN)_5H_2O]''' + OH' + HCN$ (cf. A., 1927, 1157). The displacement is dependent only on the light intensity, and does not obey the law of mass action. The photochemical effect is greatest at 440—450 $\mu\mu$. H. F. GILLBE.

Photochemical cells with complex cyanides of nickel or platinum. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, Suppl., 14—15; cf. preceding abstract).—A cell containing potassium nickelocyanide or platinocyanide yields an *E.M.F.* expressed by $\pi=\lambda(1-e^{-kt})$ during illumination and $\pi=\lambda e^{-k't}$ when the illumination is stopped. The *E.M.F.* may be due to the temporary formation of some kind of concentration cell by a change of complex dissociation or by polymerisation of complex ions or molecules. H. F. GILLBE.

Electrochemical behaviour of silicate glasses. V. Electrical properties of the anode layers. J. B. FERGUSON, M. J. MULLIGAN, and J. W. REBBECK (J. Physical Chem., 1928, 32, 1018—1030; cf. this vol., 713).—The electrical properties of various glasses with anode layers have been investigated at temperatures up to 100°. Electrolysis of a sample of glass with a sparingly soluble anode material such as mercury shows a decrease in current as electrolysis proceeds, due to a counter *E.M.F.* set up and to an increase in true resistance of the sample itself. At low voltages, the counter *E.M.F.* may nearly equal the voltage applied, but at high voltages it tends to a constant value, and the minimum voltage required in this case increases as electrolysis proceeds. The resistance of a mercury anode glass layer is many times greater than that of the original glass and changes with temperature according to the rule of Rasch and Hinricksen (A., 1908, ii, 149). With soluble anode materials, the current shows little change during electrolysis when the applied *P.D.* is constant. The smaller counter *E.M.F.* of constant value obtained under such conditions are chemical in origin. The electrical effects which accompany current reversal are described for silicate glasses with mercury-containing anode layers. Hopkinson's experiment on residual charge (Phil. Trans., 1877, **167**, 599) has been repeated under new conditions. L. S. THEOBALD.

Reactions of lead in the lead accumulator. W. SEITH (Z. Elektrochem., 1928, **34**, 362—363).—Investigations have been made with a cell consisting of a plate of radioactive lead (negative) and one of inactive lead (positive) immersed in 30% sulphuric acid. During the usual charge and discharge processes inactive lead is transferred to the positive plate. The same result is obtained when a stream of inert gas is bubbled through the cell on open circuit, the electrolyte having previously been saturated with inactive lead sulphate. The effect is ascribed to interchange between surface lead atoms and lead ions in the electrolyte, and the occurrence of this phenomenon has been demonstrated by other methods. The quantity of lead thus exchanged appears to be proportional to the concentration of lead in the electrolyte, independent of the direction of the current flow, and greater at the lead plate than at the lead dioxide plate. H. F. GILLBE.

Overpotentials produced by films of hydrogen less than one molecule thick. A. L. MCAULAY and D. P. MELLOR (Nature, 1928, **122**, 170—171).—With a mercury cathode, *N*-sulphuric acid as electrolyte, and currents of the order of 1 micro-amp./cm.^{2}, overpotentials of 0·3—0·4 volt were produced when less than one eighth of a unimolecular layer of hydrogen had been deposited. Complete elimination of oxygen was essential. A. A. ELDRIDGE.

Metal overvoltage measurements with the cathode-ray oscillograph. E. NEWBERY (Proc. Roy. Soc., 1928, A, **119**, 680—686; cf. J.C.S., 1917, **111**, 470).—The author's previous work on metal overvoltages, carried out with the aid of a rotating commutator, has been checked by measurements with the cathode-ray oscillograph. The apparatus was identical with that previously described with the exception of the electrode vessel, which was re-designed. The type of cell formerly used was found to give erroneous values for transfer resistance, although the values for overvoltage were correct. The electrodes used were copper, silver, zinc, cadmium, mercury, lead, iron, nickel, and cobalt, and the electrolytes were *N*-solutions of the corresponding metallic sulphates (for iron, ferrous and ferric sulphates), except in the case of silver, lead, and mercury, where the nitrates were used. The results show that overvoltage and transfer resistance do not occur unless a gas is being liberated at the electrode. Hydrogen is always deposited along with the metals of the iron group when these are separated electrolytically from pure solutions of their respective salts, and this gives rise to hydrogen overvoltage at the cathode. The reason for the retarded deposition of the metals of the iron group is discussed, and it is shown that the hydrated ion theory, previously suggested by the author, accounts for the observed facts. Glasstone's hypothesis, that the metals are primarily deposited in a metastable form which has a different electronic arrangement from the ordinary form, appears to be very improbable.

L. L. Bircumshaw.

Disperso-electricity. H. G. Bos (Chem. Weekblad, 1928, **25**, 259—263; cf. *ibid.*, 45, 66).—The factors which determine the maximum dispersion potential (dispersel Δ) are considered theoretically, and are the primary effect, q_I, the specific secondary effect, k, the partial tertiary effect, L, as well as the conductivity of the gases, capacity of the apparatus, etc. When q_I is nil, the value of the dispersel Δ reaches vanishing point with an earthed vessel whatever the values of the other factors; it is thus possible to remove risk of fire when spraying inflammable fluids in those cases in which admixture of another material will reduce the value q_I to zero.

S. I. Levy.

Homogeneous gas reactions. II. Introduction of quantum theory. L. S. Kassel (J. Physical Chem., 1928, **32**, 1065—1079).—Theoretical. The theory of unimolecular reactions previously advanced (this vol., 372) is extended by the introduction of quantised degrees of freedom, and the case of quantum oscillators of a single frequency, and that of two frequencies the quotient of which is an integer, are developed. When applied to the decomposition of nitrogen pentoxide, the theory accounts for the rate of this reaction at moderate pressures, but not so satisfactorily for the rate at the lowest pressures investigated. It is also applied to the decomposition of azomethane.

L. S. Theobald.

Homogeneous reaction between hydrogen and oxygen. C. H. Gibson and C. N. Hinshelwood (Proc. Roy. Soc., 1928, **A**, **119**, 591—606; cf. this vol., 483).—The kinetics of the reaction between oxygen and hydrogen have been investigated between 500° and 600°, porcelain reaction vessels being substituted for silica. The results confirm those previously obtained. Above 500°, a homogeneous reaction of high and variable order comes into prominence; the temperature coefficient is high, and at high temperatures and pressures the reaction is retarded by increasing the surface exposed to the gases. The rate is approximately proportional to the cube of the hydrogen concentration and to a power of the oxygen concentration which is greater than unity. Steam, argon, nitrogen, and helium accelerate the reaction markedly, the effect of the inert gas being nearly the same at all stages of the reaction and, for pressures up to 400 mm., increasing linearly with its concentration. The accelerating influence is roughly in the order 5 : 4 : 3 : 1. The results are interpreted by assuming that reaction chains are propagated through the gas. The chains are broken by deactivation of molecules in a heterogeneous reaction at the walls of the vessel, and lengthened by the presence of the inert gases, which increase the time during which any molecule in the gas phase escapes contact with the walls. The order of effectiveness of the inert gases can be correlated with the diffusion coefficients. Oxygen and hydrogen may exert an "inert gas effect" in addition to their normal mass action effects as participants in the reaction. Consideration of this throws some light on the nature of the reaction chains, and a working hypothesis of the mechanism of the reaction is constructed. The conditions affecting the transfer of internal energy from one molecule to another in collisions are discussed.

L. L. Bircumshaw.

Combustion of hydrocarbons; hydroxylation and/or peroxidation. W. A. Bone (Nature, 1928, **122**, 203—204).—It is considered that normally and chiefly the combustion process is one of hydroxylation and not peroxidation, although the latter mechanism is not excluded. The evidence supporting this view is summarised.

A. A. Eldridge.

[Combustion of hydrocarbons.] A. Egerton (Nature, 1928, **122**, 204).—The behaviour of anti-knocks and pro-knocks is more easily understood if the first step in the combustion process is assumed to be the temporary formation of a peroxide. Such a process does not necessarily involve dissociation of oxygen molecules.

A. A. Eldridge.

Propagation of flame in mixtures of natural gas and air. H. F. Coward and H. P. Greenwald (U.S. Bureau of Mines Tech. Paper, No. 427, 28 pp.; cf. A., 1927, 834).—The differences in properties of methane–air and natural gas–air mixtures with regard to the initiation and propagation of flame and the limits of inflammability have been investigated. The natural gas was composed of paraffin hydrocarbons, chiefly methane, with not more than 3% of nitrogen. Since certain properties, *e.g.*, limits of inflammability, follow the mixture rule, allowance can be made for the variations in composition which natural gas may show. Natural gas ignites somewhat more readily than methane, whether ignited by the hot walls of a quartz tube, a nickel bar, or an electric spark. With quartz, the ignition temperature is 15—55° lower, according to the proportion of inflammable gas present, and the time lag of ignition in the natural gas and air is shorter. With a nickel bar as the source of ignition, the ignition temperature is 30° lower throughout the whole range than that of methane, but 400—500° higher than in a quartz tube. A weaker electric spark is required to ignite natural gas and the percentage of natural gas in the most sensitive mixture (7·3—8·6%) is less than that required with methane. The limits of inflammability of natural gas in air are slightly less than those for methane. The maximum speed of uniform movement of flame for natural gas in air is greater than that for methane and less natural gas is required. Details are given of experiments in a tube 100×1 ft. to determine the speeds of uniform movement of flame in natural gas, methane, ethane, propane, and butane separately. The results for methane confirm those obtained by Mason and Wheeler (J.C.S., 1917, **111**, 1050) except for a difference in speed of 9 cm./sec. near the lower limit of inflammability.

L. S. Theobald.

Effect of alkali-metal compounds on combustion. C. A. Thomas and C. A. Hochwalt.—See B., 1928, 556.

Explosions not generally guarded against. W. P. Jorissen (Chem. Weekblad, 1928, 25, 228—230).—The explosion limits for mixtures of air and ammonia, with and without small proportions of inflammable gases, and of other mixtures not generally recognised as explosive, have been determined under various conditions. Dichloroethylene has definite and fairly wide explosion limits with air. Trichloroethylene is non-explosive in air, but lowers the explosion limits of combustible gases.

S. I. Levy.

Rate of decomposition of nitrogen pentoxide at very low pressures. A. G. Loomis and D. F. Smith (J. Amer. Chem. Soc., 1928, 50, 1864—1869).—Objections are raised to the method of Hirst and Rideal (A., 1926, 32); the experiments were repeated at 30° in an improved apparatus. The results show that at very low pressures adsorption and occlusion effects involve a large fraction of the gas present; the sudden increase in velocity at these pressures observed by Hirst and Rideal is probably nonexistent (cf. Hibben, A., 1927, 948). All previously published information on this decomposition rate is considered to be questionable. S. K. Tweedy.

Active nitrogen. V. Decay of the nitrogen afterglow. E. J. B. Willey (J.C.S., 1928, 1620—1629; cf. A., 1926, 893; 1927, 431, 1038).—Photometric studies of the decay of the nitrogen afterglow indicated that the process is bimolecular with respect to the glow-producing system between the pressures of 2 and 8 mm., a result which agrees with the statements of Angerer (A., 1921, ii, 257) and Bonhoeffer and Kaminsky (A., 1927, 801). Kinetically, however, the reaction is of the fifth order, and it is suggested that this is due to the occurrence of an initial termolecular reaction, $2N+N_2=N_2^A+N_2^B$, followed by two rapid bimolecular reactions, $N_2+N_2^A=N_2^C+N_2^D$ and $N_2+N_2^B=N_2^E+N_2^F$. F. J. Wilkins.

Velocity of thermal decomposition of malonic acid. J. Laskin (Trans. Siberian Acad. Agric. Forestry, 1926, 6, No. 1, 7 pp.; Chem. Zentr., 1928, i, 1254).—The thermal decomposition of malonic acid is unimolecular; the velocity coefficient at 138° is 0·021. A. A. Eldridge.

Velocity coefficient for bimolecular reactions in solution. D. H. Peacock (Nature, 1928, **122**, 131—132; cf. Kassel, this vol., 598).—If activated molecules of solute are deactivated by collision with solvent molecules, the latter may acquire a higher velocity, or be themselves activated, or radiation may be emitted. The consequences of these postulates are discussed. The number of activated molecules present may not be given by the usual expression $e^{-E/RT}$ for complex organic substances; "electron tautomerism," with the activated and ordinary forms in equilibrium, may prevail. The velocity of reaction would then depend on the life of the activated molecules. Conditions in a solution are favourable to the stabilisation of such "tautomerides." A. A. Eldridge.

Reactions in liquid hydrogen sulphide. IV. Thiohydrolysis of esters. A. W. Ralston and J. A. Wilkinson (J. Amer. Chem. Soc., 1928, **50**, 2160—2162).—The following esters of thioacetic acid were prepared by Obermeyer's method (A., 1888, 124): methyl; ethyl, b. p. 115—116°; propyl; *iso*propyl, b. p. 122—123°; n-*butyl*, b. p. 134—135°; *phenyl*, b. p. 110—111° (8 mm.). These esters are thiohydrolysed in liquid hydrogen sulphide into free acid and mercaptan; the degree of hydrolysis, determined by conductivity measurements, increases with the mol. wt. of the ester, and even at −77° is several times the value for the hydrolysis of the analogous oxygen esters in water at the ordinary temperature.

S. K. Tweedy.

Velocity of decomposition of tribromoacetic acid in water. O. De Groote (Bull. Soc. chim. Belg., 1928, 37, 225—239).—The velocity of decomposition of tribromoacetic acid in water has been measured by following the rate of evolution of carbon dioxide, the decrease of acidity, and the variation of the conductivity of the solution. The decomposition occurs through the intermediate formation of the tribromoacetate ion. The velocity is independent, at least in dilute solution, of the concentration of hydrogen ion. F. J. Wilkins.

Alkaline hydrolysis of esters in aqueous-alcoholic solution. II. Interaction of phenoxides and aliphatic esters. E. S. Gyngell (J.C.S., 1928, 1784—1785; cf. A., 1926, 1134; Smith, A., 1927, 213).—The expression deduced earlier for the rate of alkaline hydrolysis of esters in aqueous-alcoholic solution has been applied with satisfactory results to a series of aliphatic esters. In all cases, except for the esters of oxalic acid, the reaction proceeded as a result of the hydrolysis of the phenoxide.

F. J. Wilkins.

Velocity of esterification of nitrobenzoic acids in ethylene glycol and of naphthoic acids in glycerol. A. Kailan and E. Krakauer (Monatsh., 1928, 49, 347—384).—The velocities of esterification of the nitrobenzoic acids in ethylene glycol and of the naphthoic acids in glycerol, each in presence of water and catalysed by hydrogen chloride, were measured at 25°, and the coefficients are expressed as empirical functions of the concentrations of water (*w*) and of hydrogen chloride (*c*). The coefficients increase proportionally to *c* in glycerol and glycol containing little water and in glycerol containing more water, but more rapidly in ethylene glycol containing more water (cf. Kailan and Melkus, A., 1927, 749). Combining new with earlier results (cf. Kailan and Lipkin, A., 1927, 1148), the ratios of the coefficients for benzoic acid to those for *o*-, *m*-, and *p*-nitrobenzoic acids at $c=1/6$ and $w=0{\cdot}065$, are, in alcohol, 1 : 0·054 : 0·57 : 0·70 : 0·39 : 1·00; in glycol, 1 : 0·038 : 0·69 : 0·79 : — : — ; in glycerol, 1 : 0·068 : 0·63 : 0·80 : 0·61 : 0·93. The steric hindrance of the *o*-nitro-group is thus less in glycerol and greater in ethylene glycol than in alcohol, causing more rapid esterification in glycerol than in glycol. At small values of *c* the velocities are less in glycerol than in alcohol, but at higher values greater, owing to the greater retarding action of water on the alcoholic solution. The esterifications are all practically complete: the reverse reaction is thus inconsiderable.

The velocities of chlorohydrin formation in absence and in presence of the acids (cf. Kailan and Goitein, A., 1927, 1187) are determined, and employed to correct the values from which the velocities of esterification are calculated.

At 183° the naphthoic acids are esterified in glycerol, without mineral acid, and give "sesquimolecular" coefficients which are about 20% less in presence of 2 g.-mols. of water per litre than when anhydrous glycerol is used. In the latter, the ratios of $k_{1\cdot5}$ for benzoic and α- and β-naphthoic acids are 1 : 0·109 : 0·090, showing that benzoic acid must be more strongly dissociated than even α-naphthoic acid (on the assumption that the esterification is catalysed by hydrogen ions).

The following solubilities are given (at 25°, in g.-mols./litre of anhydrous solvent): *p*-nitrobenzoic acid in glycol, 0·08; α- and β-naphthoic acids in glycerol, 0·0175 and 0·0190, respectively.

E. W. WIGNALL.

Velocity of esterification of monoaminobenzoic acids and of pyridine-1- and 2-carboxylic acids in glycol and in glycerol. A. KAILAN and Y. M. DIAB (Monatsh., 1928, **49**, 316—346; cf. Kailan and Lipkin, A., 1927, 1148).—The velocity of esterification at 25° of *o*-, *m*-, and *p*-aminobenzoic acids and of pyridine-1- and -2-carboxylic acids in anhydrous and moist ethylene glycol and in anhydrous glycerol in presence of hydrogen chloride as catalyst has been measured; the measurements were extended to moist glycerol for *m*- and *p*-aminobenzoic acids and for nicotinic acid. The relationship between the unimolecular velocity coefficients, the water content (*w*) of the medium, and the excess of the concentration of hydrochloric acid over that of the organic acid or that of the ester (*C′*) is expressed by an empirical formula for the three last-named acids. Chlorohydrin formation must be taken into account in all cases for the anhydrous media and this coefficient has the value $4{\cdot}5$—$6{\cdot}0\times10^{-5}$. The velocity coefficients increase more rapidly in anhydrous and moist glycol and in glycerol than both the concentration of the total and of the "free" hydrogen chloride.

The velocities in glycol and in glycerol are compared with those in ethyl alcohol (Kailan, A., 1907, ii, 242). The effect of water is practically the same in glycol and in glycerol, but is less than in ethyl alcohol. The steric effect of the amino-group in the *ortho*-position is greater in glycol and less in glycerol than in ethyl alcohol. Under comparable conditions the velocity coefficients of nicotinic and picolinic acids are approximately 4 : 1 in glycol and glycerol and approximately 2 : 1 in ethyl alcohol. The differences between the velocity of esterification of benzoic acid and of the three aminobenzoic acids are practically the same in ethyl alcohol, glycol, and glycerol. Thus for $C'=1/3$ and $w=0{\cdot}03$ the ratios of the velocity coefficients of benzoic acid and *o*-, *m*-, and *p*-aminobenzoic acids are in ethyl alcohol 1 : 0·013 : 0·66 : 0·70, in ethylene glycol 1 : 0·010 : 0·67 : 0·82, and in glycerol 1 : 0·015 : 0·66 : 0·91.

I. VOGEL.

Kinetic salt effect. I. Reaction between sodium monochloroacetate and sodium thiosulphate. A. N. KAPPANNA (J. Indian Chem. Soc., 1928, **5**, 293—298).—The reaction between sodium thiosulphate and sodium monochloroacetate has been studied at 50°, 60°, and 70°. A satisfactory bimolecular velocity coefficient is obtained, which, in accord with Brönsted's theory of ionic reactions, increases as the total ionic concentration increases. The temperature coefficient is 2 in the neighbourhood of 60°. The coefficient which measures the ionic effect is practically independent of the temperature between 50° and 70°, but decreases rapidly between 25° and 50°. Alkali chlorides, sulphates, and nitrates increase the velocity coefficient, the ionic effect increasing in the order lithium, sodium, ammonium, potassium, and sulphate, nitrate, chloride.

H. F. GILLBE.

Water concentration and the rate of hydrolysis of sucrose by invertase. J. M. NELSON and M. P. SCHUBERT (J. Amer. Chem. Soc., 1928, **50**, 2188—2193).—Hydrolysis measurements on aqueous-alcoholic solutions of sucrose containing invertase indicate that the water concentration is the primary factor influencing the velocity of hydrolysis, the alcohol and sucrose concentrations being of minor significance when the sucrose concentration exceeds 20%. The affinity constant of invertase for sucrose, as measured by the method of Michaelis and Menten (A., 1913, i, 540), is inaccurate, the disturbing factor possibly being the change in water concentration.

S. K. TWEEDY.

***ortho*-Effect and reactivity. I. Magnitude and cause of the *ortho*-effect in the hydrolysis of aromatic esters.** K. KINDLER [with K. G. ELLINGER] (Annalen, 1928, **464**, 278—292).—The total effect of a radical R in the *ortho*-position with respect to carbethoxyl in a benzene nucleus is a summation of two effects: (1) the influence of R on the strength of attachment of the whole aryl grouping to the carbethoxyl group, shown in previous papers to determine the rate of hydrolysis of the ester (A., 1927, 55, 338), and (2) the direct influence of R as a centre of unsaturation on the carbonyl group. It is possible to determine the second, or "*ortho*"-effect as follows: The *ortho*-effect is negligible in esters of the type $R{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2Et$. The strength of attachment (*a*) of phenyl, that (*b*) of $R{\cdot}C_6H_4{\cdot}$, that (*a′*) of styryl, and that (*b′*) of $R{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}$ are found to be connected by the equation $\sqrt{a}:\sqrt{b}=a':b'$. By determining the rates of hydrolysis of a series of *o*-substituted benzoic and cinnamic esters it is thus possible to calculate (*b*), and so determine the direct *ortho*-effect. For R=F, Cl, Br, I, and NO_2, the relative strengths of attachment of $R{\cdot}C_6H_4{\cdot}$ to the carbethoxyl group are given by the figures

18·2, 25·2, 10·6, 15·8, and 1·91, respectively, the relative *ortho*-effects of R being given by the figures 1, 2, 5, 7·5, and 11, respectively. These last figures assume more importance when expressed on the basis of Cl=35·5, when they become 17·8, 35·5, 88·8, and 133 for the four halogens.

New experimental work includes the measurement of the velocity coefficients for the alkaline hydrolysis of the following esters: ethyl *o*- and *p*-fluoro-, *o*-chloro-, *o*-bromo-, *o*-iodo-, and *o*-nitro-benzoates; *ethyl* o-*fluorocinnamate* (b. p. 140—141°/11 mm.; o-*fluorocinnamic acid* has m. p. 175°, corr.), *ethyl* p-*fluorocinnamate*, m. p. 30—32°, b. p. 135—140°/11 mm. (*p*-fluorocinnamic acid has m. p. 208°, corr.), ethyl *o*- and *p*-bromo-, *o*- and *p*-iodo-, and *m*-amino-cinnamates.

The cause of the *ortho*-effect is discussed. It is not steric in origin and is attributed to the unsaturated nature of the group in question. The strongly unsaturated nitro-group has a particular large *ortho*-effect. E. E. TURNER.

Carbon dioxide cleavage from acetonedicarboxylic acid. E. O. WIIG (J. Physical Chem., 1928, **32**, 961—981).—The decomposition of acetonedicarboxylic acid in various solvents alone and with catalysts has been investigated between 0° and 60°. The reaction obeys the unimolecular law, is practically independent of the nature of the walls of the reaction vessel, and is not autocatalysed by acetone, a product of the decomposition. The reaction rates in water, aniline, and various alcohols permit no relationship to be expressed between velocity of reaction and specific properties of the solvent. The curve obtained by plotting *k* against mol. fractions for mixtures of *iso*propyl alcohol and water is symmetrical about a maximum value of *k* at equimolecular composition. Small amounts of water catalyse the decomposition in the alcohol and *vice versa*. With water as solvent, the decomposition is catalysed by various nitrogen bases, especially aniline, and in both water and *iso*propyl alcohol, the efficient catalysts all contain the amino-group, but no relation between catalytic activity and the strength of the base could be detected. Contrary to the demands of Taylor's theory of negative catalysis, ethyl bromide increases the rate of reaction in aniline, the velocity coefficient rising to a maximum and then decreasing as the concentration of ethyl bromide increases. Increasing concentration of hydrochloric acid decreases the rate of decomposition in water at 50° to a constant value. Neutral salts such as potassium bromide, sodium nitrate, and sodium chloride have no effect, sodium sulphate produces a slight acceleration, and salts which hydrolyse to give an alkaline reaction increase the reaction rate. Gelatin and egg-albumin, but not starch, have an accelerating effect. The temperature coefficients in the various solvents have been determined. They decrease as temperature increases and with addition of a catalyst. The critical increments vary but slightly with temperature for a given solvent, but are different with the various solvents and also with the catalysts. A mechanism of the reaction, postulating the formation of an unstable intermediate compound of the formula $(CH_2{\cdot}CO_2H)_2CO{\cdot}X$, where X is the catalyst, is discussed, together with explanations of the observed decrease in percentage decomposition with a fall in temperature. L. S. THEOBALD.

Synthesis of ammonia by the electric discharge in the presence of mercury. A. J. A. VAN DER WYK (J. Chim. phys., 1928, **25**, 251—289).—An apparatus is described for measuring the rate of formation of ammonia from its elements under the action of a silent electric discharge in presence of mercury, which acts as one of the electrodes. The influence of the area of the mercury surface, the rate of flow of the gases, the composition of the gaseous mixture, and the presence of oxygen in the gases has been studied. In any series of experiments with the same gaseous mixture the initial velocity of the reaction depends on the gaseous mixture employed in the previous series, but finally becomes constant and characteristic of the series. It is concluded that the reaction is heterogeneous and that there is intermediate formation of a hydride of mercury which is decomposed by the nitrogen. The formation and properties of this hydride are discussed. The reaction is unimolecular with respect to hydrogen and atomic with respect to nitrogen. The optimum reaction velocity is reached when the composition of the reactants is $2H_2:N_2$. W. A. RICHARDSON.

Oxidation of ferrous hydroxide in sodium hydroxide solution by means of air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, **3**, 137—141).—A current of air was drawn through a suspension of ferrous hydroxide in sodium hydroxide solution and the quantity of ferric hydroxide determined by dissolving in acid and titrating with permanganate. The reaction velocity coefficient *k* is independent of the quantity of ferrous hydroxide present and its value is identical with that for the oxidation of sodium sulphite and stannous hydroxide in alkaline solution. The value of *k* is only slightly affected by temperature, but decreases with increasing concentration of sodium hydroxide, since the velocity is probably determined by the speed of dissolution of oxygen, which is decreased by the sodium hydroxide. S. J. GREGG.

Relationship between the velocity of deposition of radium-*F* and the condition of the precipitating metal. G. TAMMANN and C. WILSON (Z. anorg. Chem., 1928, **173**, 137—155).—Copper and nickel precipitate all radium-*F* atoms which come into contact with their surfaces, whereas with silver and soft iron the precipitation is incomplete. The precipitation velocity is greater for the hard form of a metal than for the soft, and whilst for the base metals it is proportional to the concentration of the radium-*F*, for noble metals it is approximately proportional to the square root of the concentration. Gold, palladium, and platinum, and the copper–silver and silver–gold alloys, adsorb radium-*F* to double the extent when hard than when soft. Radium-*F* is precipitated by active chromium, but to only a slight extent by the passive metal; the same is true of alloys of chromium with ferromagnetic metals. H. F. GILLBE.

Dissolution and hydration velocities of kieserite. B. UEBLER (Mitt. Kali-Forschungs-

Anst., 1927, 45—69; Chem. Zentr., 1928, i, 736—737).—The velocity of dissolution of a particular specimen of kieserite is increased by diminution of grain size only down to the natural fineness. Generally, kieserite dissolves the more rapidly the purer it is; anhydrite, however, has no marked effect. The dissolution velocity in a solution unsaturated with respect to magnesium sulphate increases with rise of temperature; the hydration velocity in a solution saturated with respect to magnesium sulphate becomes maximal at about 40°, and then falls to zero at 68°. In connexion with the effect on the velocity of dissolution of the presence of various salts in the solvent, three groups are differentiated: (*a*) dilute solutions of alkali chlorides and sulphates, in which the velocity is greater than in water, (*b*) concentrated solutions of alkali chlorides and sulphates, magnesium chloride, and saturated magnesium sulphate solutions, in which the velocity is smaller than in water, (*c*) equilibrium solutions and concentrated magnesium chloride solutions, in which the velocity is smaller than the velocity of hydration in saturated magnesium sulphate solution. For the evaluation of a kieserite (*a*) the apportionment between various grades of fineness, and (*b*) the content of impurities (particularly sludge-forming) are important. In four cases grinding increased the dissolution velocity by 20—400%. The technical significance of the results is discussed.

A. A. ELDRIDGE.

Decomposition of clays. L. WASILEWSKI (Przemysł Chem., 1928, **12**, 40—48).—The velocity of evolution of ammonia from a mixture of kaolin and ammonium sulphate rises up to a temperature of 360°, after which it drops sharply almost to zero; at this point, the mixture still contains about 3·7% of ammonia, and its aqueous extract contains almost exclusively ammonium alum. At 430° the velocity of evolution of ammonia again rises; this velocity is variable, depending on the quantity of impurities, particularly iron, present, and does not correspond with the decomposition temperature of pure ammonium alum or its mixture with alumina. Thus, using clays containing 0·5% Fe_2O_3, the mixture still contains ammonia after being heated at 450° for 10 hrs., whilst where 7% of ferric oxide is present the elimination of ammonia is complete within 4 hrs. Pure ammonium alum retains its ammonia even more tenaciously, a considerable portion remaining even after heating at 550°. If the clay–ammonium sulphate mixture be heated at 350—370°, about 0·5% of the ammonia present is oxidised, and the product still contains about 3·7% of ammonia, which is evolved at 450°, at which temperature, however, about 9% of the ammonia is oxidised to nitric acid.

R. TRUSZKOWSKI.

Silver-ion catalysis of persulphate oxidations. III. Oxidation of ammonium ion. IV. Oxidation of oxalate ion. C. V. KING (J. Amer. Chem. Soc., 1928, **50**, 2080—2088, 2089—2099; cf. this vol., 27).—III. The reaction $NH_4^{\cdot}+4S_2O_8''+3H_2O \longrightarrow 10H^{\cdot}+8SO_4''+NO_3'$ in presence of silver ions was followed by conductivity measurements. The velocity curves are not strictly reproducible and are autocatalytic in character, indicating that, contrary to previous belief, the second reaction $4Ag^{\cdot\cdot\cdot}+NH_4^{\cdot}+3H_2O \longrightarrow 4Ag^{\cdot}+NO_3'+10H^{\cdot}$ is not immeasurably rapid. A velocity equation cannot be set up in terms suitable for experimental confirmation. Irregularities in the velocity curves of other reactions may be due to slight autocatalytic effects, especially in the case of sucrose inversion, which may proceed according to the equations: $C_{12}H_{22}O_{11},nH_2O+H^{\cdot} \longrightarrow C_{12}H_{22}O_{11},nH_2O,H^{\cdot}$; $C_{12}H_{22}O_{11},nH_2O,H^{\cdot} \longrightarrow$ invert sugar $+H^{\cdot}$. If the second reaction is slow enough the velocity curve will be slightly autocatalytic in character, owing to the accumulation of the intermediate compound (cf. Pennycuick, A., 1926, 249); if it is "instantaneous" the reaction will appear unimolecular.

IV. The oxidation of oxalate ion in dilute solution by persulphate ion, which proceeds very slowly in the absence of a catalyst, was followed in the presence of the silver ion by measurement of the rate of evolution of carbon dioxide. The catalysed reaction is much faster than the analogous oxidation of ammonia, ammonium ion, and chromium ion. Duplication of the results is very difficult to attain. The glass walls of the reaction vessel exert some catalytic effect. Some of the velocity curves are autocatalytic in character, indicating that whilst an intermediate compound sometimes accumulates, at other times it decomposes with a speed comparable with its rate of formation. Livingston suggests that the persulphate and silver ions form a relatively inactive complex which can oxidise only fairly powerful reducing agents (*e.g.*, oxalate ion, but not ammonium or chromium ions), from which a more active silver ion, $Ag^{\cdot\cdot\cdot}$ or $AgO^{\cdot}$, is formed, capable of oxidising weaker reducing agents. A series of simultaneous and consecutive reactions can then be formulated which will account for all the persulphate oxidations. Other mechanisms are suggested.

S. K. TWEEDY.

Landolt's reaction. V. Catalytic influence of sodium thiosulphate on the Dushman reaction. W. ROMAN-LEVINSON (Z. Elektrochem., 1928, **34**, 333—350).—The catalytic influence is measured in terms of the percentage increase *G* of the reaction velocity, defined by $G=100(T_S/T_{St}-1)$, where T_S is the time of reaction without thiosulphate and T_{St} the time with thiosulphate. *G* is scarcely influenced by the iodide-, iodate-, or sulphite-ion concentrations, but varies with the hydrogen-ion concentration. Four reactions are recognised: the ordinary Dushman reaction, $IO_3'+5I'+6H^{\cdot}=3I_2+3H_2O$; the Dushman *S*-reaction, in which sulphite is present; the Dushman *T*-reaction, in presence of thiosulphate; and the Dushman *S*-*T*-reaction, which is the *S*-reaction catalysed by thiosulphate. If the concentration of thiosulphate be small compared with that of sulphite the time of reaction falls with increase of thiosulphate concentration and reaches a minimum when the two concentrations become of similar magnitude; from this point it is the *T*-reaction which must be considered, the reaction velocity increasing with increase of thiosulphate concentration. The calculated velocity coefficients K' and K'' of the *S*-*T*- and *T*-reactions are $1{\cdot}86\times10^{15}$ and $1{\cdot}45\times10^{10}$, respectively. The mechanisms of the reactions are discussed.

H. F. GILLBE.

Mechanism of oxidation processes. XIV. Activation of oxygen by iron. H. Wieland and W. Franke (Annalen, 1928, **464**, 101—226).—The autoxidation of solutions of ferrous salts has been studied using sodium acetate and acetic acid as a buffer. Absorption of oxygen follows the unimolecular law. The temperature coefficient of the process is normal, whilst a change from p_{H} 5 to 7 accelerates the reaction 4- or 5-fold. At p_{H} 5, neutral salts have little effect on the rate of autoxidation, although sodium sulphate, possibly owing to its producing complex salts, causes diminution of the reaction velocity to half its previous value.

The rate of autoxidation of slightly hydrated ferrous chloride is greater in acetone than in ethyl alcohol or *iso*propyl alcohol, greater in these solvents than in methyl alcohol, and least in water.

The autoxidation of a number of acids in presence of iron salts has been studied. In general, ferrous sulphate is the added iron salt and an acetate buffer is used. Formic acid: Autoxidation of the ferrous salt induces autoxidation of formate, the latter ceasing when no more ferrous salt remains, since ferric iron does not oxidise formic acid. Lactic acid: Autoxidation of the lactate is more rapid than that of the formate, about one third of the oxygen absorbed by the system during the complete oxidation of the iron being used to oxidise the lactate to carbon dioxide, acetaldehyde, and (some) pyruvic acid. Autoxidation is most rapid at p_{H} 8·0, and is slower in air than in pure oxygen. Pyruvic acid: This case is very similar to that of lactic acid; in neither case does ferric iron oxidise the acid. Tartaric (or racemic) acid: This autoxidation is investigated very fully. Small changes in conditions very greatly affect the progress of the reaction. Ferric salts do not initiate autoxidation of tartaric acid, but play a considerable part in the autoxidation of tartaric acid in presence of ferrous salts, since the dihydroxymaleic acid formed is oxidised by ferric, producing ferrous salts. The autoxidation proceeds much further in acid than in neutral solution, and has a normal temperature coefficient up to 20°. At 30°, however, the process is not appreciably quicker than at 20°. To some extent, the process is catalytic in nature, owing to the reduction of ferric salt by the dihydroxymaleic acid formed. The last acid acts as a strong positive catalyst for a similar reason. The autoxidation process is greatly accelerated by sodium sulphate and somewhat accelerated by sodium nitrate or by cupric sulphate, whilst sodium chloride, bromide, and iodide act as strong decelerants. *p*-Benzoquinone also has a decelerating influence. Increased pressure of oxygen accelerates autoxidation, but the total amount of oxygen used is less than is the case with lower pressures (cf. Annalen, 1927, **457**, 20).

Dihydroxymaleic acid: Owing to the sparing solubility of the sodium and potassium salts of this acid, buffering is best effected using acetic acid and lithium acetate. The spontaneous decomposition of a buffered (p_{H} 4·8) solution of the acid (nitrogen atmosphere) is markedly accelerated by ferrous salts. Substitution of phthalate for acetate as buffer has only a slight effect. Phosphate produces marked deceleration, and addition of pyrophosphate in addition further decelerates the velocity of autoxidation (cf. Warburg, A., 1915, i, 337). Buffering with glycine causes acceleration. At p_{H} 1·4 and 13, autoxidation is markedly slower than at intermediate acidities, p_{H} 5 being the optimum condition for the process. The spontaneous autoxidation of dihydroxymaleic acid in absence of iron proceeds more rapidly in alkaline than in acid solution. The main reaction here involved is: $CO_2H\cdot C(OH){:}C(OH)\cdot CO_2H \xrightarrow{\frac{1}{2}O_2} CO_2H\cdot CO\cdot CO\cdot CO_2H$, not that taking place as in Fenton's experiments (giving glycollaldehyde, carbon dioxide, and water), which occurs in acid solution in presence of ferric salts. Ferric salts oxidise dihydroxymaleic acid (p_{H} 5, lithium acetate and acetic acid) to diketosuccinic acid, which during the autoxidation process gives oxalic (1/3) and mesoxalic acid (2/3), the latter slowly giving oxalic acid.

Glyceric acid: This case is similar to that of tartaric acid. Added ferrous salt produces an effect roughly proportional to its concentration. Thioglycollic acid: Copper salts are in general more positively catalytic of the autoxidation of this acid than are those of iron, but the latter become the more effective in the neighbourhood of the neutral point. Sulphuric acid is a product of autoxidation, which is decelerated by cyanides.

Quinol: The oxidation of this substance by ferric salts renders the autoxidation of quinol in presence of ferrous salts similar to that of dihydroxymaleic acid. The velocity of change depends very largely on p_{H}. Near the neutral point, ferrous salts reduce *p*-benzoquinone, so that the basis of the autoxidation process is: $OH\cdot C_6H_4\cdot OH + 2Fe^{\cdot\cdot\cdot} \rightleftharpoons O{:}C_6H_4{:}O + 2Fe^{\cdot\cdot} + 2H^{\cdot}$. The buffer used may have a considerable effect on the mobility of the equilibrium. Thus, autoxidation is particularly facile in presence of a sodium acetate buffer, less so with sodium glycerate, and much less so with sodium phthalate. The catalytic action of iron salts in this process has its optimum within certain fairly narrow limits of concentration. *p*-Benzoquinone has a marked decelerating effect on the autoxidation of quinol, probably owing to the formation of an inactive iron–quinhydrone complex. As regards the mechanism of the autoxidation: it is difficult to recognise the process as one of true catalysis, and it may be that ferric salt is the effective oxidant of the quinol. This would explain why in the slow autoxidation of quinol that occurs in absence of a buffer, ferrous and ferric salts produce effects of a similar magnitude. In buffered solutions, ferrous iron is more powerful in action than ferric iron, so that probably an oxygen activation process is at work, in this case, on the part of a ferrous salt–acetate complex.

Pyrocatechol: Here the accelerative influence of iron in autoxidation is markedly stronger than with quinol. Pyrogallol: This case is similar to that of pyrocatechol, but autoxidation is more rapid. The product is not purpurogallin, but is the amorphous brown substance, resembling a humic acid, obtained in the hydrogen peroxide–iron oxidation of pyrogallol. Potassium ferrocyanide aids autoxidation, but to a much smaller extent than simple iron salts.

Experiments have been carried out on the autoxidation of dihydroxymaleic acid in complete absence of iron salts, in order to see if the known absorption of oxygen by solutions of the acid is really due to the presence of unsuspected traces of iron. The conclusion is reached that whilst special purification of the acid (vacuum distillation in quartz vessels) renders it more stable in this respect, iron is not the initiator of the process, but merely catalyses a reaction in progress. This is substantiated by the fact that in neutral solutions of the purified material cyanide slightly accelerates autoxidation, whereas in presence of traces of iron it markedly diminishes the acceleration due to the latter.

Similar results have been obtained with quinol. The autoxidation of quinol itself produces hydrogen peroxide at p_H 3·6, whilst when iron is present no peroxide is formed.

Arsenious acid: According to Manchot (A., 1901, ii, 549) one equivalent of oxygen is activated during the oxidation of Fe^{II} to Fe^{III}, and is used for the conversion of arsenite into arsenate. This is not actually realisable under all conditions of acidity. The most concentrated weakly alkaline (p_H 6) solutions of arsenite obtainable show an activation of only 0·88 equivalent. For p_H 10, corresponding with $NaAsO_2$, activation corresponds with 0·6 equivalent, and for more strongly alkaline solutions, corresponding with Na_2HAsO_3, it corresponds with not more than one equivalent, in opposition to Gire's results (A., 1920, ii, 544). When alkalinity corresponds with Na_3AsO_3, activation exceeds 1 equivalent of oxygen, the extra (½ mol.) activation being due to spontaneous autoxidation and not to oxidation of arsenite by ferric salt.

Hypophosphorous acid: This acid is not appreciably oxidised by oxygen in absence of iron salts. The autoxidation in presence of iron salts seems to be an induction effect, ceasing when all ferrous salt has become oxidised. It is little affected by p_H. The results appear to show that the activation of molecular oxygen by ferrous salts cannot be due to the intermediate formation of a peroxide, as suggested by Manchot (*loc. cit.*). It is probable that the first stage in the autoxidation is the formation of a complex between the ferrous salt and the hypophosphite, rendering the hydrogen of the latter more active as regards oxidation. The second stage is the very slow reaction $2Fe^{III}+H_3PO_2 \longrightarrow 2Fe^{II}+H_3PO_3$. Phosphorous acid behaves similarly to hypophosphorous, but the activation is less pronounced and is more influenced by the acidity conditions.

Certain combined autoxidations have been studied. The autoxidation of hypophosphorous acid in presence of ferrous salts and dihydroxymaleic acid is catalytic in type, the p_H of the solution not greatly affecting the rate of change. (In absence of iron salts, solutions of mixed hypophosphorous and dihydroxymaleic acids do not absorb oxygen.) Diketosuccinic acid (not tartaric or glyceric acid) behaves similarly to dihydroxymaleic acid, but it is only slowly oxidised by ferric salt, whereas the latter acid is instantaneously oxidised by ferric salt in presence of hypophosphorous acid. The mechanism of the combined autoxidation is discussed. Possibly a readily dehydrogenated ferric salt–diketosuccinic acid complex is formed intermediately, but no final explanation can be reached on the existing evidence.

The autoxidation of formic acid in presence of ferrous salts is accelerated by dihydroxymaleic acid, but the acceleration is less than in the above case of hypophosphorous acid. Diketosuccinic acid is again an active intermediate. Relatively large amounts of dihydroxymaleic acid are required to produce acceleration, and the same is the case in the autoxidation of lactic acid in presence of ferrous salts. Dihydroxymaleic acid produces no acceleration of the autoxidation of quinol–ferrous salts.

The autoxidation of formic acid–ferrous salt in presence of thioglycollic acid is similar to the above case of formic–dihydroxymaleic acid. The experiments of Szent-Györgyi (A., 1924, i, 708, 1284) have been extended and put on a quantitative basis. Thioglycollic acid does not accelerate autoxidation until present in a certain concentration, but after this is reached its effect is proportional to its concentration. When lactic acid replaces formic acid there is a more pronounced mutual activation, whilst when tartaric replaces formic acid, less thioglycollic acid is required to accelerate the (more rapid) autoxidation.

The autoxidation of hypophosphorous acid and ferrous salt in presence of thioglycollic acid is a case of true catalysis, due to the equilibrium between ferric iron–thioglycollic acid and ferrous iron–dithiodiglycollic acid. This equilibrium must lie mostly on the ferrous iron side because of the marked initial activation (by thioglycollic acid) which precedes the main, catalytic, stage. Activation is ascribed to the formation of a thioglycollic acid–ferrous salt complex.

The autoxidation of hypophosphorous acid in presence of ferrous salts is not accelerated by pyruvic acid, but the autoxidation of pyruvic acid in presence of hypophosphorous acid is markedly accelerated by traces of ferrous salts, giving a case of true catalysis (ferrous salt–hypophosphorous acid complex).

Some consideration is given to cases of direct addition of oxygen to an unsaturated linking, as distinguished from the above cases, in which hydrogen is removed from a substance. The work of Meyerhof (Pflüger's Archiv, 1923, **199**, 531) on the autoxidation of linolenic acid, as accelerated by thioglycollic acid, has been extended. The autoxidation is further accelerated in presence of iron salts, in absence of which it is not rapid; it ceases when the whole of the thioglycollic has passed into dithiodiglycollic acid. In presence of traces of iron, the process is catalytic in type. The autoxidation of linolenic acid has now been studied in a buffered (p_H 4·6) solution. Ferrous iron greatly accelerates this process, but ferric iron does not do so until it has been in progress for some time. More marked acceleration is produced in presence of thioglycollic, dihydroxymaleic, or diketosuccinic acid.

The autoxidation of lecithin (cf. Meyerhof, *loc. cit.*) at p_H 4·6, in presence of ferrous salts, is catalytic in nature. In presence of ferric salts an induction effect is predominant. Added dihydroxymaleic acid produces marked acceleration, diketosuccinic acid causes deceleration when present in small, but acceleration when present in larger, quantities, whilst thioglycollic acid accelerates the reaction when it is present in small amounts and accelerates to a proportionally smaller extent when its quantity is increased.

Figures are also given for the autoxidation of crude linoleic acid under different sets of conditions.

E. E. TURNER.

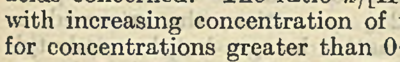
Catalytic action of neutral salts. Effect of normal alkali sulphates on alkali acid sulphates in the ketonic splitting of ethyl acetoacetate. E. A. GOODHUE and H. L. DUNLAP (J. Amer. Chem. Soc., 1928, **50**, 1916—1922).—The decomposition of ethyl acetoacetate in acid solution at 80°, 90°, and 95° was investigated in a special apparatus in presence of *N*-potassium and sodium sulphates and the corresponding hydrogen sulphates (0·2*N* and 0·4*N*). The reaction proceeds at approximately half the speed when both normal and acid sulphates are present as compared with the rate when acid sulphate only is used.

S. K. TWEEDY.

Inversion of sucrose interpreted by the dualistic theory of catalysis and by activity of hydrogen ions. M. DUBOUX and R. MERMOUD (Helv. Chim. Acta, 1928, **11**, 583—597; cf. A., 1924, ii, 842).—The inversion of sucrose has been studied polarimetrically at 0°, using as catalysts 0·091—3·6*N*-hydrochloric acid and 0·74—3·69*N*-nitric acid. The velocity coefficients have been calculated from the usual logarithmic formula and the hydrogen-ion concentrations from known conductivity data of the acids concerned. The ratio $k/[H^{\cdot}]$ increases rapidly with increasing concentration of the acid used, and for concentrations greater than 0·1*N* no proportionality exists between k and $[H^{\cdot}]$. Contrary to the demands of the dual theory of catalysis, the values of k_H and k_M in the equation $k=k_H[H^{\cdot}]+k_M(C-[H^{\cdot}])$ are not independent of the concentration of acid, neither is k_H independent of the nature of the acid. On the other hand, for hydrochloric acid as catalyst, k is proportional, as a first approximation, to the activity of the hydrogen ions a_H, according to the equation $k=k'_H a_H$. This agrees with Moran and Lewis' views of the mechanism of the inversion (J.C.S., 1922, **121**, 1613), but not with the hypothesis of Colin and Chaudun (A., 1927, 835).

L. S. THEOBALD.

Mechanism of tautomeric interchange and effect of structure on mobility and equilibrium. III. Function of alkaline and acid catalysts in the mutarotation of derivatives of tetramethylglucose. J. W. BAKER (J.C.S., 1928, 1979—1987; cf. this vol., 870).—The influence of acid and alkaline catalysts on the mutarotation of a series of *p*-substituted anilides of tetramethylglucose of the type



$\mathrm{NHR{\cdot}CH{\cdot}[CH{\cdot}OMe]_3{\cdot}CH{\cdot}CH_2{\cdot}OMe}$ (CH and CH joined through O)

has been studied. For acid catalysts, the relative velocities of mutarotation of these derivatives run parallel with the strengths as bases of the compounds NH_2R. Further, anilides of tetramethylglucose mutarotate more rapidly than the less basic derivatives of tetra-acetylglucose. It is suggested that these acid catalysts act by inducing a positive charge on the nitrogen atom which facilitates the liberation of the attached proton. With alkaline catalysts a minimum velocity of mutarotation is found at an intermediate position in the series. The following m. p. of the anilides of tetramethylglucose are recorded: p-*bromoanilide,* 154°; p-*chloroanilide,* 141°; p-*toluidide,* 151°; p-*anisidide,* 110°.

F. J. WILKINS.

Mechanism of chemical change. I. Promotion and arrest of the mutarotation of tetra-acetylglucose in ethyl acetate. T. M. LOWRY and G. G. OWEN (Proc. Roy. Soc., 1928, **A**, **119**, 505—522).—Reasons are given for the special suitability, for the study of the mechanism of chemical change, of reactions which give rise to mutarotation. A technique is developed for producing at will arrests of mutarotation. It was found possible to prepare "clean" solutions of tetra-acetylglucose in ethyl acetate in a silica flask which had been ignited in a furnace and allowed to cool in a desiccator. Under these conditions it was often found that the solution in the flask remained unchanged for some days, although the samples usually underwent a more or less rapid mutarotation when transferred to a polarimeter tube for observation. When the polarimeter tube was first filled with solution, a certain value was obtained for the velocity coefficient of the reaction; on refilling after 24 hrs., however, the rate was about 0·1 of its original value, showing that the cleanliness of the tube was increased enormously by contact with the clean solution. Further experiments showed that the addition of a drop of water to the clean solution in the flask was not sufficient to initiate mutarotation, but that water containing a trace of acid or alkali was an extremely efficient catalyst. In these catalysed solutions, however, a maximum velocity of mutarotation was developed only after 2 or 3 hrs., giving rise to inflected curves in place of the usual unimolecular type, as if the action had been resolved into two consecutive stages. The occurrence of these inflected curves is probably conditioned by the use of highly purified materials and clean apparatus. In the case of the alkaline catalyst, there is evidence that the action may be due to catalysis by the contaminated surface of the containing vessel. The progressive acceleration of the change might be due to the development of some sort of chain reaction, spreading from this surface into the interior of the liquid. Experimental details are given for the cleaning of the silica polarimeter tube, the purification of phosphoric oxide, and the preparation of dry ethyl acetate. The sugar was carefully dried in a desiccator. The source of light was an enclosed mercury arc, and all readings were made with the green line Hg 5461 Å. Special experiments showed that the light from the arc had no influence on the course of mutarotation.

L. L. BIRCUMSHAW.

Autoxidation and antioxygenic action. Catalytic properties of phosphorus compounds. C. MOUREU, C. DUFRAISSE, and M. BADOCHE (Compt. rend., 1928, **187**, 157—161).—The catalytic oxygenating activities of phosphorus trichloride, phosphorus oxychloride, phosphorus tribromide, phosphorus oxybromide, hypophosphorous acid, phosphorous acid, phosphoric acid, and several substituted phosphines have been investigated with respect to benzaldehyde and other substances. The results, particularly those obtained with phosphoric acid, are discussed in the light of the theory that an oxygenating catalyst must be a substance itself susceptible of further oxidation. C. W. Gibby.

Electrodynamics of surface catalysis. A. K. Brewer (J. Physical Chem., 1928, **32**, 1006—1017).—Theoretical. On the basis of previous experimental work (A., 1926, 1074; Proc. Nat. Acad. Sci., 1927, **13**, 574) concerning the emission of ions during various surface catalysed reactions, a mechanism of surface catalysis, treated as a special case of thermionic emission in gases, is advanced. The electrostatic image and intrinsic surface forces, together with the kinetic energy of agitation, dissociate the molecules of gas on the surface into ions, which are driven from the surface by kinetic agitation with a probability distribution of velocities. Chemical reaction then results from a combination of the ions of which the velocity components perpendicular to the surface are sufficient to carry them to a region of weak surface forces, which is the chemically active region. The rate of the forward reaction, developed from an electrodynamic point of view, can be represented by the equation $dC/dt=A'T^{n'/2}e^{-b'/T}$, where A' is a combination factor and b' is the complete chemical work function, the work done by the ions escaping sufficiently from the surface to react. The reverse reaction can be similarly represented, but with different values of the constants, and equilibrium is expressed by the equation $K=(A'/A'')T^{(n''-n')/2}e^{-(q-b')/T}$.

L. S. Theobald.

Catalysts of the reaction $CO+H_2O \rightleftharpoons CO_2+H_2$. W. Dominik (Przemysł Chem., 1928, **12**, 229—235).—The following equation is derived whereby the catalytic power b of a catalyst for the reaction $CO+H_2O \rightleftharpoons CO_2+H_2$ may be calculated: $b=V/[(K-1)(x_1-x_2)]\times \log_e[(x-x_2)/(x-x_1)][(x_0-x_1)/(x_0-x_2)]$, where b is constant for a given temperature and size of grain of the given catalyst, K is the velocity coefficient of the above reaction, V the velocity of flow of the reaction mixture in c.c. per hr. per g. of catalyst, x and x_0 are the partial pressures of carbon dioxide respectively during and before the reaction, and x_1 and x_2 the roots of the equation $x(p_0H_2+x-x_0)/\{p_0CO-(x-x_0)\}\{p_0H_2O-(x-x_0)\}-K=0$. The values of b are shown experimentally to be constant for a gas mixture of the above type.

R. Truszkowski.

Catalysis in the conversion of allyl alcohol and acraldehyde into propaldehyde. P. E. Weston and H. Adkins (J. Amer. Chem. Soc., 1928, **50**, 1930—1935).—The proportion of acraldehyde, as compared to that of propaldehyde, formed when allyl alcohol is passed over a zinc oxide catalyst, is the greater the slower is the rate of flow of the alcohol, indicating the possibility of the reaction (1) $CH_2{:}CH{\cdot}CHO+CH_2{:}CH{\cdot}CH_2{\cdot}OH=CH_3{\cdot}CH_2{\cdot}CHO+CH_2{:}CH{\cdot}CHO$. The reaction (2) $CH_2{:}CH{\cdot}CH_2{\cdot}OH=CH_3{\cdot}CH_2{\cdot}CHO$ (cf. Constable, A., 1927, 27) probably does not take place because the following reaction, in which (2) could not occur, takes place in presence of aluminium oxide: $CH_2{:}CH{\cdot}CHO+PrOH=2Et{\cdot}CHO$.

S. K. Tweedy.

Catalytic hydrogenation of unsaturated compounds. III. S. V. Lebedev and A. O. Jakubtschuk (J. Russ. Phys. Chem. Soc., 1928, **60**, 793—828).—Curves expressing velocity of catalytic absorption of hydrogen by various unsaturated hydrocarbons containing conjugated double linkings are constructed. The velocity is constant for di*iso*propenyl up to 69% of the total hydrogen necessary for saturation (termed the critical point); the curve rises and then falls sharply at 91%, after which the reaction proceeds to completion at a low velocity. The rise represents the hydrogenation of *as*-methyl*iso*propylethylene, and the third section the hydrogenation of tetramethylethylene. At 69% saturation, the reaction mixture contains no di*iso*propenyl, 38% of di*iso*propyl, 45% of *as*-methyl*iso*propylethylene, and 17% of tetramethylethylene. The quantities of all substances formed during the process of hydrogenation lie on straight lines joining the origin to various points lying on the ordinate of the critical point. Fully saturated molecules are formed from the very beginning of the reaction and are, up to the critical point, formed exclusively from the original substances. Mono-substituted ethylenes added to substances possessing conjugated double linkings such as di*iso*propenyl, isoprene, divinyl, and piperylene absorb hydrogen together with the latter substances up to the critical point, whence it follows that where such mono-substituted ethylenes are formed during the first stage, they will undergo further hydrogenation before the critical point is reached. The critical point of divinyl is at 72% saturation, the intermediate products of hydrogenation being *n*-butylene, *ψ*-butylene, and butane. The critical point of piperylene is at 73% saturation, and the products are propylethylene, *s*-methylethylethylene, and *n*-pentane. The nature of the products formed and their relative quantity are unaffected by the presence of substituted ethylenes in the reaction mixture.

R. Truszkowski.

Catalytic decomposition of oleic acid. B. M. Marks and H. C. Howard, jun. (J. Physical Chem., 1928, **32**, 1040—1048).—The catalytic activity of nickel towards oleic acid over the range 200—490° has been investigated. The results are best interpreted as a combination of specific catalytic and thermal effect. The main gaseous product is carbon monoxide and the predominating reaction can be represented by the scheme $2nC_{17}H_{33}{\cdot}CO_2H \longrightarrow nC_{17}H_{34}+(C_{17}H_{32})_n+2nH_2O+2nCO$. Analytical data for the reaction products are given.

L. S. Theobald.

Reduction of oxygen at a mercury dropping-cathode. J. Heyrovský (Časopis Českoslov. Lék., 1928, 7, 242—251; Chem. Zentr., 1928, i, 1149).—Measurements of the current as a function of the polarisation potential for dilute solutions of electrolytes, *e.g.*, potassium chloride or sulphuric acid, in contact with air, show that the oxygen is first reduced to hydrogen peroxide at a potential corresponding approximately with that of the normal calomel electrode. The influence of p_H on this reduction potential is very small. The second stage, the reduction to water, takes place in $0{\cdot}001N$-hydrogen ion solution at $-0{\cdot}60$ volt. A. A. Eldridge.

Formation of perchlorate during electrolytic production of chlorate. A. V. Pamfilov and O. S.

Fedorova (J. Russ. Phys. Chem. Soc., 1928, **60**, 765—770).—Differences observed between the results of analysis of the gases evolved and of the reaction solution in the electrolytic production of chlorates are partly due to the formation of perchlorate.

R. Truszkowski.

Preparation of metallic alloys by electrolysis of aqueous solutions of binary electrolytes. I. Copper and cadmium. N. N. Efremov (Ann. Inst. Polyt. Ural, 1927, **6**, 111—148).—Only with certain complex compounds, such as the cyanides, is it found possible to obtain conditions giving the necessary levelling of potentials for the simultaneous separation of copper and cadmium by electrolysis. Investigation has been made of: the curves of the electrode potentials Cd|Cd(CN)$_2$ and Cu|CuCN, especially in regard to the content of potassium cyanide and to the current density; the working conditions requisite for the realisation of the electrolysis; the dependency of the current efficiency on various factors, and the most suitable materials for anode and cathode. Characteristic of the copper–cadmium alloys is the change in magnitude of the electrode potentials. The curve for copper lies almost throughout above the curve for cadmium, so that the interval of common separation is greatly narrowed; cadmium, which is deposited before copper, produces no depolarising action. Any excess of potassium cyanide in the electrolyte results in the separation of cadmium alone. Use of a copper–cadmium anode does not result in deposition of the alloy on the cathode, owing to the tardy solubility of the anodic material. The current efficiency varies little with the temperature of the bath, but increases markedly with the current density, a value 0·4—0·6 amp. per 100 cm.^{2} giving a good deposit and a high yield. With lower current densities, the brittleness of the resulting alloys increases, whilst with higher, the bath undergoes rapid exhaustion and deposition of pulverulent metal sets in. The relation between copper and cadmium in the anodic alloy scarcely affects the separation, the proportions of the two metals in the electrolyte being dependent principally on the proportion in the electrolyte. It is therefore preferable to employ an insoluble anode, such as platinum, but even then, not more than 10—12% of the bath must be used up. Moreover, soluble anodes favour slimy deposits. Since electrolytic copper–cadmium alloys alloy well with platinum, copper, cadmium, iron, lead, aluminium, zinc, and other metals, these may readily be plated in this way. If subsequent removal of the alloy from the cathode is necessary, a zinc cathode coated with graphite and then with a thin layer of cadmium or copper should be used. Tricadmium dicupride, Cd_3Cu_2, which is a stable exothermic compound, decomposes extremely readily on anodic dissolution, and it would be of interest to ascertain if this behaviour is general with intermetallic compounds and if any of these are capable of unchanged cathodic deposition.

T. H. Pope.

Influence of p_H on the electrolytic deposition of copper in presence of gelatin. C. Marie and M. L. Claudel (Compt. rend., 1928, **187**, 170—171).—Copper sulphate has been electrolysed in presence of gelatin in solutions of p_H 0·88—3·57. A deposit consisting of copper sulphate, gelatin, and water is obtained, and, at p_H 3·2, reaches a maximum weight of about 6% of the weight of copper deposited in a comparison cell. This is paralleled by the maxima which the viscosity, swelling, and osmotic pressure of gelatin pass through at about the same p_H.

C. W. Gibby.

Anodic behaviour of copper–antimony alloys. H. Neumark.—See B., 1928, 611.

Addition agents in electrodeposition. V. Application of the complex cation theory of crystalloidal addition agents to base metals. I. G. Fuseya and K. Murata. **II.** G. Fuseya and R. Yumoto.—See B., 1928, 611.

Corrosion and anodic polarisation of iron. R. A. Dengg and H. J. Donker (Korrosion u. Metallschutz, 1927, **3**, 241—248; Chem. Zentr., 1928, i, 749).—Inconclusive experiments on polarisation of various types of iron and steel in an electrolyte of 0·1*N*-potassium chloride and 0·1*M*-potassium carbonate are described, and the bearing of the results on corrosion is discussed. A. A. Eldridge.

Nature of the deposit formed during electrolysis of neutral and alkaline solutions with an antimony cathode. J. Grant (J.C.S., 1928, 1987—1988).—Analyses of the deposit obtained in the cathode compartment during the electrolysis of neutral or alkaline solutions with an antimony cathode indicate that it is not, as Weeks and Druce (A., 1925, ii, 700) suggest, a solid hydride of antimony (Sb_2H_2), but finely-divided antimony containing 0·01—0·25% of adsorbed hydrogen. F. J. Wilkins.

Direct electrolytic preparation of potassium permanganate. G. Rapin (Compt. rend., 1928, **187**, 112—114).—The preparation of potassium permanganate by electrolysis of aqueous potassium hydroxide or carbonate with a silicomanganese anode has been investigated. The anode must be compact; pulverised silicomanganese invariably leads to the formation of manganese dioxide. If potassium carbonate is used, the solution finally contains only potassium permanganate, but if potassium hydroxide is used it contains potassium silicate also. Raising the temperature increases the efficiency. Too high a concentration of potassium hydroxide causes the formation of potassium manganate.

C. W. Gibby.

Electrolytic oxidation of aniline. J. Sládek (Časopis Českoslov. Lék., 1927, **7**, 299—312; Chem. Zentr., 1928, i, 1171—1172).—The oxidation of aniline to benzoquinone in presence of sulphuric acid with a lead anode, and the influence of different catalysts, current strength, temperature, anode surface, and quantity of electrolyte are discussed. The benzoquinone can be determined by Knecht and Hibbert's method. Vanadium pentoxide is the best catalyst. The electrolysis is continued for 23 hrs., with a current density of 1 amp./dm.^{2}, the temperature not exceeding 10°. A. A. Eldridge.

Electrolytic reduction of nitrosoantipyrine. M. Giordani (Annali Chim. Appl., 1928, **18**, 289—296).—The progress of the electrolytic reduction of nitroso-to amino-antipyrine is studied by comparing the amounts of gas evolved at the cathode of the electrolytic cell and in a voltameter; apparatus for the comparison, and the effects of change of cathode, of current density, and of concentration are described. A spongy nickel cathode is the most effective; the amino-compound (separated as benzylidene derivative) is obtained in 65% yield. E. W. WIGNALL.

Influence of intensity of illumination on velocity of photochemical union of bromine and hydrogen, and determination of the mean life of a postulated catalyst. F. BRIERS and D. L. CHAPMAN (J.C.S., 1928, 1802—1811; cf. A., 1926, 484; Bodenstein and Lütkemeyer, A., 1925, ii, 218).—For very high light intensities the rate of union of hydrogen and bromine is approximately proportional to the square root of the intensity, whilst for low light intensities the rate of reaction is directly proportional to the intensity. The total amount of chemical change is not solely dependent on the total time of illumination for light of constant intensity, but alters when the illumination is rendered intermittent. From a quantitative study of this effect the mean life of the commonly assumed catalysts (either atoms or active molecules) has been estimated to be 0·063 sec. F. J. WILKINS.

Photochemical reaction between bromine and tartaric acid in aqueous solution. II. III. Mechanism of the reaction. J. C. GHOSH and K. P. BASU (J. Indian Chem. Soc., 1928, **5**, 342—360, 361—372).—II. The reaction in the dark between aqueous bromine and tartaric acid solutions is negligible compared with that in the light, which is characterised by a long induction period, high quantum efficiency, and a temperature coefficient of the velocity of 4·6 for 10° rise of temperature. At constant bromine concentration, increase of tartaric acid concentration results in an increase of the induction period, whilst at constant tartaric acid concentration increase of bromine concentration produces a small reduction of the induction period, but a considerable diminution of the unimolecular velocity coefficient. Sodium hydrogen tartrate greatly accelerates the reaction and decreases the induction period. By addition of hydrogen bromide at the commencement of the reaction the relatively small increase of the hydrogen-ion concentration during the reaction results in only a small decrease of the reaction velocity, whereas normally the hydrogen bromide produced during the reaction causes a rapid decrease of velocity.

III. The observed phenomena are explained by assuming as the mechanism of the reaction the sequence: (*a*) bromine molecules are photochemically activated, (*b*) part of the active bromine atoms react with oxygen present in the system, and, in the initial stages, part are used up in destroying photo-inhibitors, (*c*) the remaining active bromine atoms produce photobromination of the tartaric acid. H. F. GILLBE.

Products of the photochemical decomposition of azoimide. A. O. BECKMAN and R. G. DICKINSON (J. Amer. Chem. Soc., 1928, **50**, 1870—1875).—Brief illumination by ultra-violet radiation causes 27% of the azoimide to decompose into nitrogen and hydrogen, and the remainder into nitrogen and ammonia (the latter forming ammonium azide). By means of the quartz-fibre and McLeod gauges the mol. wt. of azoimide is found to be 43·6±2·1. S. K. TWEEDY.

Photochemistry of silver halides. I. Gravimetric determination of excess silver in photographic layers. II. Decomposition of photographic layers with neutral, acid, and alkaline hydrogen peroxide, and with ammoniacal ammonium sulphide. H. H. SCHMIDT and F. PRETSCHNER.—See B., 1928, 625.

Conversion of maleic acid into fumaric acid by bromine atoms. F. WACHHOLTZ (Z. physikal. Chem., 1928, **135**, 147—181).—See this vol., 492.

Basis of the selective chemical action of *X*-rays and light. L. SIMONS (Brit. J. Radiol., Roentgen Soc. Sect., 1927, **23**, 124—134).—There is very little variation in the ionisation produced by complete absorption of corpuscular radiation in a number of organic vapours, hydrogen, air, and sulphur dioxide, *i.e.*, there is no selective action. In the absorption of a light quantum, with *X*-rays varying in wavelength over the critical *K*-range for silver, no selective change was observed in the average energy of the photo-electrons. The observed selective rise in absorption is due to an increase in the number of atoms thus ionised. The primary ionisation in which selective effects are shown is always negligible in comparison with the total ionisation, which includes ionisation by impact. For a mixed substance, the chemical change will be proportional to the product of the true absorption coefficient of the whole and the energy density of the *X*-rays at each point. CHEMICAL ABSTRACTS.

Photochemical decomposition by *X*-radiation. R. GLOCKLER and O. RISSE (Z. Physik, 1928, **48**, 845—851).—The liberation of oxygen from dilute aqueous solutions of hydrogen peroxide and of potassium persulphate when the solution was exposed to radiation of wave-lengths 1540, 710, 560, 190 X. was examined. The amount of oxygen liberated is independent of the wave-length when the conditions of experiment are so chosen that the fraction of the energy of the *X*-ray beam which is effective for the liberation of electrons is constant. For 0·0017*N*-solutions the amount of this energy associated with the decomposition of 1 g.-mol. of hydrogen peroxide and of potassium persulphate is 70,000 and 17,500 g.-cal., respectively. R. W. LUNT.

Mechanism of chemical reactions. H. J. TAYLOR (Proc. Amer. Phil. Soc., 1926, **65**, 90—98).—Evidence is adduced in support of the view that certain reduction processes, especially in the presence of excited mercury vapour, depend on the intervention of hydrogen atoms. CHEMICAL ABSTRACTS.

Separation of krypton and xenon from atmospheric air. A. LEPAPE (Compt. rend., 1928, **187**, 231—234).—The sources of loss in the separation of krypton and xenon from air are discussed. Good yields have been obtained by fractional adsorption on coconut charcoal or silica gel, at the b. p. of oxygen. C. W. GIBBY.

Action of mixtures of salts on copper. A. Launert (Compt. rend., 1928, **187**, 206—207).—The changes produced in the density and specific resistance of copper by heating in mixtures of salts have been investigated and can be explained by absorption of the vapours of the salts. The mixtures used were potassium chloride–strontium chloride, potassium chloride–barium chloride, and barium chloride–strontium chloride at temperatures below their eutectic points. C. W. Gibby.

Reactions in the solid state. IV. Compounds resulting from the reaction between basic and acidic oxides and carbonates and the mode of compound formation. W. Jander (Z. anorg. Chem., 1928, **174**, 11—23).—Barium carbonate and tungstic oxide heated together in any proportion in a platinum crucible at 700° in a current of carbon dioxide for 2 hrs. yield always normal barium tungstate, holding in solution a small quantity of tungstic oxide. Molybdenum trioxide and barium carbonate, and tungstic oxide and calcium carbonate, under similar conditions, yield only normal barium molybdate and calcium tungstate, respectively. Lead monoxide heated with tungstic oxide or molybdenum trioxide at 600—650° yields normal lead tungstate or molybdate, in both cases a small quantity of lead monoxide remaining in solution in the salt. When heated with excess of silicon dioxide at 950°, barium carbonate yields principally barium metasilicate, whilst if the barium carbonate be in excess the orthosilicate is the main product. The conditions necessary for chemical reaction between two solid substances are stated and discussed. H. F. Gillbe.

Mercuric tetramminopersulphate. F. Fichter and S. Stern (Helv. Chim. Acta, 1928, **11**, 754—758; cf. Tarugi, A., 1903, ii, 481).—Mercury (10 g.), ammonium persulphate (20 g.), and concentrated ammonia solution (50—60 c.c.) react vigorously, yielding crystals of mercuric tetramminopersulphate, $[Hg^{\cdot\cdot}(NH_3)_4]S_2O_8$, which loses ammonia in air, but can be recrystallised from concentrated ammonia solution. Mercuric acetate or nitrate, but not the chloride or cyanide, can replace the mercury used as starting material. The salt prepared by Tarugi (*loc. cit.*) is considered to be identical with this salt and not a mercurous derivative. Hydrolysis results in a mixture of basic salts of varying composition.

L. S. Theobald.

Ionium from Fergan ores. A. N. Pilkov (J. Russ. Phys. Chem. Soc., 1928, **60**, 835—841).—Ionium is separated from other elements by adsorption on cerium oxalate, after precipitation of uranium, radium, and other radioactive elements. R. Truszkowski.

Corroding action of sodium fluosilicate on aluminium. G. M. Kraay (Arch. Rubbercultuur, 1928, **12**, 141—143; Med. Proefstat. v. Rubber, No. 30, 81—83).—Aluminium is slowly dissolved by a 0·1% solution of sodium fluosilicate with the evolution of hydrogen. In a 0·5% solution of the same salt corrosion is much less rapid and after a short time ceases altogether owing to the formation of a protective coating. Aluminium pans can therefore be used for the coagulation of latex with sodium fluosilicate. A. R. Powell.

Phosphorescent aluminium nitride activated by silicon. E. Tiede, M. Thimann, and K. Sensse (Ber., 1928, **61**, [*B*], 1568—1573).—Aluminium nitride is prepared by the action of ammonia on particularly pure, technical aluminium contained in a molybdenum boat heated at 1300° in a nickel tube. Admixture with silicon is obtained by adding the required amount of silica to the metal previously to its conversion into the nitride. Alternatively, the nitride is prepared by allowing the vapour of the compound $AlCl_3,NH_3$ to come into contact with a tungsten spiral heated electrically at above 1000°. Addition of silicon is effected by use of silicon tetrachloride. The presence of about 0·5% of silicon is requisite for the production of phosphorescence. The optimum amount is 5%, but this limit can be greatly exceeded before the power to phosphoresce is lost. The iron arc or mercury lamp are the best exciting sources. Cathode rays cause a dark blue luminescence. Röntgen rays and feeble radium preparations have no effect. Emission is chiefly in the blue region; three bands appear, thus giving a close analogy with the boron nitride–carbon phosphors. The distinct blue afterglow persists for about a minute and then gives place to a pale, whitish phosphorescence. Specimens of aluminium nitride which have been exposed to a high temperature but scarcely phosphoresce by reason of their low silicon content become distinctly green when exposed to the iron arc; the colour disappears when they are preserved in the dark, but can be renewed by fresh exposure. It is remarkable that whereas graphitic carbon is the excitant of the graphitic boron nitride, the diamond-like aluminium nitride is excited only by diamond-like silicon.

H. Wren.

Effect of temperature on the optical properties of kaolinite. T. N. McVay (J. Amer. Ceram. Soc., 1928, **11**, 224—226).—Euhedral crystals of kaolinite, contained in small platinum boxes, were heated in a platinum-wound tube furnace. Samples were taken from the furnace at different temperatures and afterwards examined microscopically. Up to 600° no change, other than a slight cloudiness at the edges, was observed. At 620° a uniaxial form, which was retained up to 1400°, was produced. These crystals, probably Rinne's metanacrite, were cloudy and seemed to be broken into very thin plates. Under strong illumination interference figures were noticeable. Both the cloudiness and the interference figures vanished when the crystals were held at 1450° for 2 hrs. However, under this treatment, a development, showing a cross-hatched appearance with small crystals arranged in rhombs, became evident. These crystals were probably mullite, but they were so minute that no optical determinations could be made. The anticipated change in the nature of the substance at 900° was not observed. A. T. Green.

Rare earths. J. Švéda (Časopis Českoslov. Lék., 1927, **7**, 226—232; Chem. Zentr., 1928, i, 1162).—The decomposition of praseodymium and neodymium oxalates in a current of oxygen as a function of time and temperature was investigated. The product always contains carbonate. Praseodymium oxalate decomposes the more rapidly, but in a mixture containing the oxides in equal amounts the reverse is the case. The praseodymium salt yields an oxide of composition corresponding with Pr_6O_{11}, which when heated in a vacuum yields the sesquioxide, whilst the neodymium salt yields only Nd_2O_3. The presence of neodymium does not inhibit the formation of the oxide Pr_6O_{11}. A. A. Eldridge.

Neodymium selenate. J. A. N. Friend and A. A. Round (J.C.S., 1928, 1820—1822).—Neodymium selenate, $Nd_2(SeO_4)_3$, has been isolated, together with the corresponding *penta-* and *octa-hydrates.* Evidence for the existence of a dodecahydrate has been obtained. F. J. Wilkins.

Chemical reactions in the electrodeless discharge. S. S. Bhatnagar, R. K. Sharma, and N. G. Mitra (J. Indian Chem. Soc., 1928, 5, 379—382).—The substance produced from naphthalene under the influence of the electrodeless discharge has the formula $C_{24}H_{20}O$. Other decompositions which have been observed are: $PbSO_4 \longrightarrow PbSO_3+PbS$; $CaSO_4 \longrightarrow CaSO_3$, $KBrO_3 \longrightarrow KBrO+KBr$, $KIO_3 \longrightarrow KI+I_2$, $KClO_3 \longrightarrow KClO+KCl$, and $PbSO_4+Mg \longrightarrow PbS+MgO_2$. H. F. Gillbe.

Reaction between nitrogen dioxide and liquid mercury. W. C. Pierce and W. A. Noyes, jun. (J. Amer. Chem. Soc., 1928, **50**, 2179—2187).—The reaction was followed by observing the time of formation, t, of a solid film on the mercury surface. The period of use of the reaction vessel and also its dimensions influence t, although the variation does not obviously depend on the surface/volume ratio of the vessel. Further, t does not depend primarily on the size of the mercury surface, but it seems to be smaller in those vessels in which dust particles from the walls can be carried direct on to this surface. Decrease in t follows the introduction of moisture or a rise in temperature. The presence of foreign gases does not influence t, but after the vessel has been in use for some time a reduction in pressure results in a reduction in t; at very low pressures t increases (cf. Moore and Noyes, A., 1924, ii, 748). Gas ions, positive or negative, accelerate the reaction when sufficient are present. Activation of the nitrogen dioxide by irradiation does not affect t. The accelerating action of light is probably due to the activation of a surface film, and seems to be associated with the photo-electric effect (cf. *loc. cit.*). S. K. Tweedy.

Preparation and properties of pure phosphorus trioxide. (Miss) C. C. Miller (J.C.S., 1928, 1847—1862).—Phosphorus trioxide prepared according to the method of Thorpe and Tutton (J.C.S., 1890, **57**, 545) contains 1·5—2% of free phosphorus. This product may be purified by fractional crystallisation from carbon disulphide, washing with light petroleum, together with subsequent volatilisation after exposure to light. The pure oxide melts at 23·8°. Further, it neither glows nor oxidises in moist or dry oxygen at the ordinary temperature and is unaffected by sunlight. F. J. Wilkins.

Action of hydrazine on quinquevalent arsenic in faintly acid solutions. H. Kubina and J. Plichta (Z. anal. Chem., 1928, 74, 235—247).—The reduction of quinquevalent arsenic by hydrazine in presence of potassium bromide has been investigated in its dependence on the acidity of the medium. In presence of hydrochloric acid the production of arsenic trichloride is quantitative only when the concentration of acid is considerable. On distillation of mixtures which are not strongly acid metallic arsenic is found in the receiver and on the condenser tube. The liquid remaining in the distillation vessel is turbid and contains free arsenic. When neutral solutions are distilled arsenic is deposited in the distillation flask, but no arsenic appears in the receiver or on the condenser tube. Addition of arsenious oxide prior to distillation causes an increased and more rapid formation of arsenic in the distillation flask, but a decreased production in the cooling arrangement. No arsenic is produced with arsenious salts alone.

It appears that when the acidity is not considerable the hydrolysis, $As^{\cdot\cdot\cdot\cdot\cdot}+4H_2O \longrightarrow AsO_4{}'''+8H^{\cdot}$, is not negligible and that part of the hydrolysed fraction is reduced to arsine. The latter reacts with arsenic trichloride produced by the normal reduction to form arsenic according to the scheme $AsH_3+AsCl_3 \longrightarrow 2As+3HCl$. This reaction occurring in the gaseous phase is responsible for the production of arsenic in the condensing apparatus. In presence of much acid the hydrolysis is repressed and reduction follows the normal course. Other reducing agents, *e.g.*, oxalates and ferrous salts, behave normally.

When acid solutions containing sulphates are distilled, arsenious sulphide and sulphur dioxide are often formed in the final stages. J. S. Carter.

Vanadium compounds and boiling sulphuric acid. A. Sieverts and E. L. Müller (Z. anorg. Chem., 1928, **173**, 313—323).—Boiling concentrated sulphuric acid effects partial reduction of vanadium pentoxide to vanadyl sulphate and partial oxidation of vanadyl sulphate to vanadium pentoxide. If more than 0·12 g. of vanadium per 100 c.c. of acid is present the salt $VOSO_4$ separates (cf. Auger, A., 1921, ii, 554). In presence of ammonium sulphate both quinquevalent and quadrivalent vanadium are completely reduced to the tervalent state by boiling concentrated sulphuric acid and the salt $NH_4V^{III}(SO_4)_2$ separates (cf. Rosenheim and Mong, A., 1925, i, 1411). Sulphuric acid and potassium sulphate decompose vanadyl sulphate into equimolecular proportions of vanadic acid and the salt $KV^{III}(SO_4)_2$ (cf. Eichner, this vol., 34). A. R. Powell.

Element 91. Properties and isolation. A. von Grosse (J. Russ. Phys. Chem. Soc., 1928, **60**, 843—845, 847—854).—See this vol., 259, 495.

Phosphorescent combustion of sulphur. H. J. Emeléus (J.C.S., 1928, 1942—1950).—Sulphur dioxide together with a small amount of sulphur trioxide are the products of the phosphorescent combustion of sulphur. No traces of any oxide of sulphur more volatile than sulphur dioxide were found and no evidence of the formation of ozone was obtained. As distinct from arsenic (A., 1927, 497), sulphur shows no "glow pressure," above which the oxidation is non-luminous. Sulphur dioxide and a series of organic vapours inhibit the glow over definite ranges of temperature, experiments with methyl salicylate demonstrating that the temperature at which the glow appears is the higher the greater is the concentration of inhibitant. F. J. WILKINS.

Molybdenum selenides and selenomolybdates. E. WENDEHORST (Z. anorg. Chem., 1928, **173**, 268—272).—From a sulphuric acid solution of ammonium molybdate hydrogen selenide precipitates brownish-black molybdenum triselenide, which dissolves in solutions of alkali hydroxides, selenides, and sulphides, giving deep red to brown solutions (cf. Moser and Atynski, A., 1925, ii, 583). If the acid molybdate solution is reduced with zinc until it becomes of a deep reddish-brown colour and is then saturated with hydrogen selenide, dense brownish-black leaflets of *dimolybdenum pentaselenide*, Mo_2Se_5, are precipitated. A mixture of molybdenum trioxide and selenium when heated in hydrogen to dull redness yields *molybdenum diselenide*, $MoSe_2$, in bluish-black, glistening leaflets insoluble in alkali solutions. When a mixture of potassium carbonate, selenium, and molybdenum dioxide is fused above 1200°, and the product leached with water, a residue of dark lead-grey crystals of *molybdenum sesquiselenide*, Mo_2Se_3, is obtained. Saturation of a solution of potassium molybdate in concentrated potassium hydroxide with hydrogen selenide results in the separation of red needles of *potassium selenomolybdate*, K_2MoSe_4. The sodium salt cannot be prepared under similar conditions, but the *ammonium* salt, $(NH_4)_2MoSe_4$, is obtained in glistening, blue crystals from a solution of molybdic acid in concentrated ammonia. All selenium compounds of molybdenum prepared in the wet way rapidly decompose on exposure to the air; their preparation must therefore be carried out in an atmosphere of nitrogen. A. R. POWELL.

Cyano-sulpho-compounds of molybdenum. E. CREPAZ (Gazzetta, 1928, **58**, 391—401).—Octacyano-salts of quadrivalent molybdenum (*e.g.*, $K_4[Mo(CN)_8],2H_2O$) were prepared by passing hydrogen sulphide intermittently through a solution containing potassium molybdate and potassium cyanide. The aquo-cyano-compound, $K_4[Mo(OH)_4(CN)_4],6H_2O$, was obtained on crystallising a solution of the octacyano-compound to which potassium hydroxide had been added. The exhaustive treatment with hydrogen sulphide of a solution of molybdic acid and potassium cyanide in potassium hydroxide solution gave a blue cyano-sulpho-compound, $K_3[MoS(CN)_4],2H_2O$, containing tervalent molybdenum. A method of determining the valency of the central metal atom in these compounds, based on the reduction by them of an ammoniacal solution of silver chloride, is described. In this reaction, for each equivalent of the compound involved two equivalents of silver are obtained as silver sulphide and (in the case of the above compound containing tervalent molybdenum) three equivalents of silver as metal. F. G. TRYHORN.

Thio-salts. VI. Complex molybdenum vanadium sulphides. L. FERNANDES (Atti R. Accad. Lincei, 1928, [vi], 7, 496—501).—The preparation and analysis of a number of new complex *sulphides*, to which the following formulæ relate, is described: $[H_2(MoS_4)_4(VS_3)_2](NH_4)_5H_3,10H_2O$;
$[H_2(MoS_4)_3(VS_3)_3[(NH_4)_5H_2,12H_2O$;
$[H_2(MoS_4)_2(VS_3)_4](NH_4)_5H,25H_2O$;
$[H_2(MoS_4)_4(VS_3)_2](Guanidine)_5H_3,15H_2O$;
$[H_2(MoS_4)_3(VS_3)_3](Guanidine)_5H_2,22H_2O$;
$[H_2(MoS_4)_2(VS_3)_2](Guanidine)_5H,15H_2O$;
$[H_2(MoS_4)_2(VS_3)_4]Tl_5H,60H_2O$.
R. W. LUNT.

Sulpho-salts. V. Additive compounds with hexamethylenetetramine. F. RODOLICO (Atti R. Accad. Lincei, 1928, [vi], 7, 660—666).—The following *compounds*, which are more stable and more easily crystallisable than the normal salts, have been prepared by a generalised method involving the addition of magnesium chloride and hexamethylenetetramine (X) to a warm solution of the alkali sulpho-salt: $MgMoO_4,X,10H_2O$; $MgMoSO_3,2X,10H_2O$; $MgMoS_2O_2,2X,10H_2O$; $MgMoS_3O,2X,10H_2O$; $MgMoS_4,2X,10H_2O$; $MgWO_4,X,10H_2O$; $MgWSO_3,2X,10H_2O$; $MgWS_2O_2,2X,10H_2O$; $MgWS_3O,2X,10H_2O$; $MgWS_4,2X,10H_2O$. From measurements of the crystallographic data for some of these compounds it was found that the morphotropic variations do not correspond with the gradual substitution of oxygen by sulphur. F. G. TRYHORN.

Per-acids of uranium, tantalum, and niobium. A. SIEVERTS and E. L. MÜLLER (Z. anorg. Chem., 1928, **173**, 297—312).—Peruranic acid may be prepared either by addition of excess of 3% hydrogen peroxide solution to a solution of uranyl nitrate or by treating uranium trioxide with hydrogen peroxide. Pertantalic and perniobic acids are obtained by treating the corresponding potassium salts in concentrated aqueous solution with the requisite quantity of sulphuric acid. The acids are finely-divided white and yellow powders, respectively, containing one atom of active oxygen to one atom of metal. Both tantalic and niobic acids dissolve in 3% hydrogen peroxide, forming opalescent solutions; pertantalic acid is precipitated by alcohol or sodium chloride from the solution, but perniobic acid cannot thus be isolated. A. R. POWELL.

Action of fluorine on aqueous solutions of chromium and manganese salts. F. FICHTER and E. BRUNNER (J.C.S., 1928, 1862—1868).—Fluorine is as effective as a platinum anode in oxidation. Chromium alum in 1·5—7·5*N*-sulphuric acid solution is oxidised even at 0° to chromic acid. Sulphur tetroxide produced by the action of fluorine on the sulphuric acid is probably the active agent. Dilute potassium dichromate solutions are reduced, the fluorine first reacting with water to form hydrogen peroxide, which gives rise to perchromic acid which loses oxygen to form chromic salts. Manganous sulphate in the presence of sulphuric acid is oxidised to a labile sulphate of quadrivalent manganese, $Mn(SO_4)_2$. F. J. WILKINS.

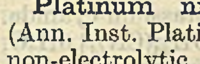
Cobalticarbonates. G. A. BARBIERI (Atti R. Accad. Lincei, 1928, [vi], 7, 747—753).—The structure of the green compound obtained by the action of an oxidising agent on a cobaltous salt in presence of alkali hydrogen carbonate is discussed. Cobaltinitrites dissolve in a warm solution of sodium hydrogen carbonate, giving an intensely emerald-green coloured solution. This contains a complex cobalticarbonate which is identical with the first-mentioned green compound and is not a mixture of compounds containing bi- and quadri-valent cobalt (cf. Metzl, A., 1914, ii, 472). The tervalent nature of the cobalt in the green solutions is further shown by isolating from them solid cobaltic compounds of known structure, *e.g.*, cobaltic acetylacetonate and purpureocobaltic chloride. O. J. WALKER.

Aquo-hexammine and -pentammine complexes of tervalent cobalt and chromium which crystallise in the cubic system. O. HASSEL and G. B. NAESS (Z. anorg. Chem., 1928, **174**, 24—30).—The complex salts, $[Co(NH_3)_6]SeO_4I$, $[Co(NH_3)_6]SeO_4Br$ (also $+3H_2O$), and $[Co(NH_3)_6]CrO_4Br,3H_2O$, have been prepared and their crystal structures studied; those of the first two differ from that of the corresponding sulphate only in the magnitude of the lattice constant, whilst that of the chromium complex corresponds with the structures of the trihydrates of hexamminecobaltic sulphatochloride and hexamminecobaltic selenatobromide. A series of complexes of tervalent chromium has been prepared, all the members of which have the cubic structure: $[Co(NH_3)_6]CrO_4I$, obtained by warming cobaltous carbonate with chromic acid solution, and heating the filtered solution, after addition of ammonia solution, with iodine; the analogous compound containing molybdenum in place of chromium could not be obtained, the sparingly soluble product having, after recrystallisation, the formula $2[Co(NH_3)_6]_2(MoO_4)_3,3H_2O$; $[Co(NH_3)_5,H_2O](ClO_4)_3$ (deep red), $[Cr(NH_3)_6](ClO_4)_3$ (yellow), and $[Cr(NH_3)_5,H_2O](ClO_4)_3$ (bright red), which belong to the octahedral system; $[Cr(NH_3)_5,H_2O]SO_4ClO_3$, which has the fluorspar-like structure of the complex sulphatobromides. The following lattice constants (Å.) have been determined: $[Co(NH_3)_6]SO_4I$, 10·71; $[Co(NH_3)_6]SO_4Br$, 10·51; $[Co(NH_3)_6]SeO_4I$, 10·79; $[Co(NH_3)_5H_2O]I_3$, 10·81; $[Co(NH_3)_5H_2O](ClO_4)_3$, 11·32; $[Co(NH_3)_5H_2O]SO_4I$, 10·62; $[Co(NH_3)_5H_2O]SO_4Br$, 10·45; $[Co(NH_3)_6]SeO_4Br$, 10·63; $[Co(NH_3)_6](ClO_4)_3$, 11·38. H. F. GILLBE.

Optical activity of platinum. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1928, **6**, 40—55).—Two of the stereoisomerides of the complex $[en\,NH_3\,Pt\,Cl_2\,NO_2]Cl$ are resolved into optical antipodes, as are the complexes $[en\,C_5H_5N\,Pt\,NO_2\,Cl_2]OH$ and $[en\,(NH_3)_2\,Pt\,Cl_2]Cl_2$. Stereoisomerism has a profound influence on the magnitude of the rotatory power and of the dispersion coefficient. The application of the amido-reaction, leading to the production of $[en\,NH_2\,Pt\,NO_2\,Cl_2]$, brings about a change of sign of rotation, the appearance or the enhancement of Cotton's effect, and an increase in the absolute value of molecular rotation. The inversion of rotation takes place with ionic velocity and is completely reversible, and the same applies to that of triammines and tetrammines. *trans*-Trichlorotriammines react with ammonia to form *cis*-dichlorotetrammines. Inversion of optical rotation is brought about by alkalis only in those complexes into the nucleus of which ammonia enters. R. TRUSZKOWSKI.

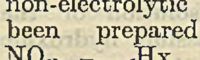
Platinum nitrites. III. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1928, **6**, 23—39; cf. *ibid.*, 1926, **4**, 243; 1927, **5**, 102).—*cis*-Nitritochloroplatinites of the general type $[A_2\,Pt\,NO_2\,Cl]$ are produced by the action of ammonia or ethylenediamine on $K_2[Pt\,Cl_3\,NO_2]$, obtained by the action of sodium nitrite on potassium chloroplatinite. The complex $[en\,Pt\,Cl\,NO_2]$ yields on treatment with excess of ammonia the base $[en\,NH_3\,Pt\,NO_2]Cl$, which with hydrochloric acid gives the base $[en\,NH_3\,Pt\,Cl_3]Cl$, which reacts with alkali hydroxides to produce the amide $[en\,NH_2\,Pt\,Cl_3]$. Where pyridine is substituted for ammonia in the above series of reactions, the trichlorotriammine base $[en\,C_5H_5N\,Pt\,Cl_3]Cl,2H_2O$ is produced, which with dilute alkalis yields $[en\,C_5H_5N\,Pt\,Cl_3]OH$; this, when dried at 140°, loses a molecule of water to form the imide $[NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{:}(C_5H_5N)PtCl_3],H_2O$. The substance $[en\,C_5H_5N\,Pt\,NO_2]Cl$ reacts in solution with chlorine to yield $[en\,C_5H_5N\,Pt\,NO_2\,Cl_2]Cl$, whence $[en\,(C_5H_5N)\,(NO_2)_2\,Cl\,Pt]Cl,2H_2O$ is derived by the action of sodium nitrite, and this product again yields with 25% ammonia $[en\,(C_5H_5N)\,(NO_2)_2\,Cl\,Pt]OH$. Ammonia substitutes only one chlorine atom of $[en\,C_5H_5N\,Pt\,NO_2\,Cl_2]Cl$, the product being $[en\,C_5H_5N\,Pt\,NH_2\,NO_2\,Cl]Cl,2H_2O$, readily convertible into $[en\,C_5H_5N\,NH_3\,Pt\,NO_2\,Cl]Cl$ by the action of hydrochloric acid. The *cis*-tetrammines yield Cleve's salt on reduction to bivalent platinum. The tetrammine $[en\,(NH_3)_2\,Pt\,NO_2\,Cl]Cl_2$ is separated into its optical antipodes, for which $[M]_D$ is $-137°$ and $+145°$, respectively. Two stereoisomerides of $[en\,C_5H_5N\,Pt\,NO_2\,Cl_2]Cl$ are prepared, and three of $[en\,NH_3\,Pt\,NO_2\,Cl_2]Cl$. When quadrivalent is reduced to bivalent platinum in these complexes the two substituent groups which are attached to one co-ordinate are invariably eliminated. R. TRUSZKOWSKI.

Platinum nitrites. IV. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1928, **6**, 55—97).—The following non-electrolytic nitrites of bivalent platinum have been prepared: *dinitrodihydroxylaminoplatinum*,



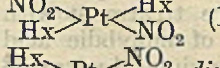
$\begin{matrix}NO_2\\Hx\end{matrix}\!>\!Pt\!<\!\begin{matrix}Hx\\NO_2\end{matrix}$

(Hx=NH_2OH), its *stereoisomeride*



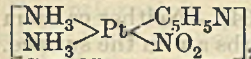
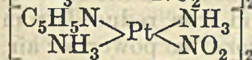
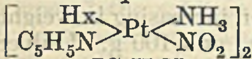
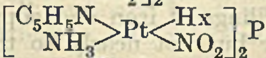
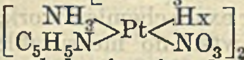
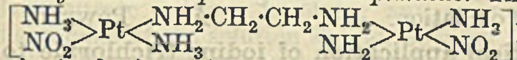
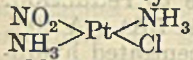
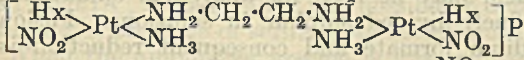
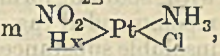
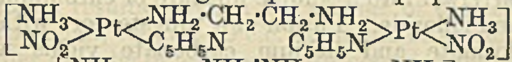
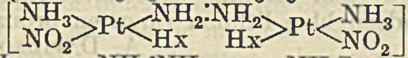
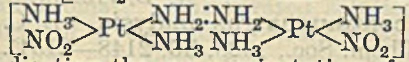
$\begin{matrix}Hx\\Hx\end{matrix}\!>\!Pt\!<\!\begin{matrix}NO_2\\NO_2\end{matrix}$,

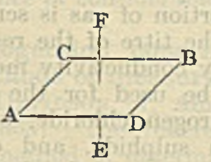
dinitroplatinumdiammine,

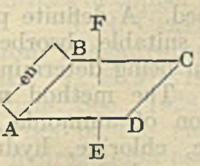


$\begin{matrix}NO_2\\NH_3\end{matrix}\!>\!Pt\!<\!\begin{matrix}NH_3\\NO_2\end{matrix}$,

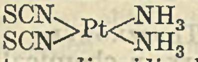
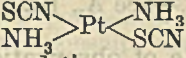
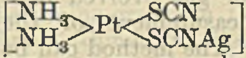
hydroxylaminodinitroplatinumammine, *pyridinodinitroplatinumammine*, *ethylenediamminodinitroplatinum*, *dihydroxylaminonitrochloroplatinum*, *hydroxylaminonitrochloroplatinumammine*, the corresponding *derivative* with pyridine substituted in place of ammonia, *pyridinonitrochloroplatinumammine*, *ethylenediamminonitrochloroplatinum*, *nitrochloroplatinumdiammine*. The following electrolytic salts of nitro-derivatives of bivalent platinum have been prepared: *trihydroxylaminonitroplatinum chloroplatinite*, *amminodihydroxylaminonitroplatinum chloroplatinite*, *diamminohydroxylaminonitroplatinum chloroplatinite*, *amminoethylenediamminonitroplatinous chloride*, *diamminopyridinonitroplatinum chloroplatinite*

 $\left[\begin{matrix}NH_3\\NH_3\end{matrix}>Pt<\begin{matrix}C_5H_5N\\NO_2\end{matrix}\right]_2PtCl_4$, and its *isomeride*  $\left[\begin{matrix}C_5H_5N\\NH_3\end{matrix}>Pt<\begin{matrix}NH_3\\NO_2\end{matrix}\right]_2PtCl_4$, *amminodipyridinonitroplatinum chloroplatinite, amminopyridinohydroxylaminonitroplatinum chloroplatinite,*  $\left[\begin{matrix}Hx\\C_5H_5N\end{matrix}>Pt<\begin{matrix}NH_3\\NO_2\end{matrix}\right]_2PtCl_4$, its *isomerides,*  $\left[\begin{matrix}C_5H_5N\\NH_3\end{matrix}>Pt<\begin{matrix}Hx\\NO_2\end{matrix}\right]_2PtCl_4,2H_2O$ and  $\left[\begin{matrix}NH_3\\C_5H_5N\end{matrix}>Pt<\begin{matrix}Hx\\NO_3\end{matrix}\right]_2PtCl_4$, and *amminopyridinomethylaminonitroplatinum chloroplatinite.* The *complex*  $\left[\begin{matrix}NH_3\\NO_2\end{matrix}>Pt<\begin{matrix}NH_2\cdot CH_2\cdot CH_2\cdot NH_2\\NH_3\qquad\qquad\qquad NH_2\end{matrix}>Pt<\begin{matrix}NH_3\\NO_2\end{matrix}\right]PtCl_4$ is obtained by the interaction of the complex  $\begin{matrix}NO_2\\NH_3\end{matrix}>Pt<\begin{matrix}NH_3\\Cl\end{matrix}$ with 1 mol. of ethylenediamine and the addition of potassium chloroplatinite. The *complex*  $\left[\begin{matrix}Hx\\NO_2\end{matrix}>Pt<\begin{matrix}NH_2\cdot CH_2\cdot CH_2\cdot NH_2\\NH_3\qquad\qquad\qquad NH_3\end{matrix}>Pt<\begin{matrix}Hx\\NO_2\end{matrix}\right]PtCl_4$ is obtained in an analogous way from  $\begin{matrix}NO_2\\Hx\end{matrix}>Pt<\begin{matrix}NH_3\\Cl\end{matrix}$, and the following complexes are prepared similarly:  $\left[\begin{matrix}NH_3\\NO_2\end{matrix}>Pt<\begin{matrix}NH_2\cdot CH_2\cdot CH_2\cdot NH_2\\C_5H_5N\qquad\qquad C_5H_5N\end{matrix}>Pt<\begin{matrix}NH_3\\NO_2\end{matrix}\right]PtCl_4$,  $\left[\begin{matrix}NH_3\\NO_2\end{matrix}>Pt<\begin{matrix}NH_2:NH_2\\Hx\qquad Hx\end{matrix}>Pt<\begin{matrix}NH_3\\NO_2\end{matrix}\right]SO_4$, and  $\left[\begin{matrix}NH_3\\NO_2\end{matrix}>Pt<\begin{matrix}NH_2:NH_2\\NH_3\ NH_3\end{matrix}>Pt<\begin{matrix}NH_3\\NO_2\end{matrix}\right]SO_4$. Formulæ indicating the space orientation of quadrivalent platinum bases are written [ABCDEFPt], where A to F represents groups substituted within the octahedron in the order shown in formulæ (I) and (II), the latter applying to ring derivatives containing ethylenediamine. The following non-electrolytic derivatives of quadrivalent platinum are prepared and described: *nitrotrichloroplatinumdiammine,* $[NH_3\ Cl\ NH_3\ NO_2\ Cl_2\ Pt]$, *pyridinonitrotrichloroplatinumammine,* $[C_5H_5N\ NH_3\ NO_2\ Cl_3\ Pt]$, and *ethylenediaminonitrotrichloroplatinum,* $[en\ NO_2\ Cl_3\ Pt]$. The following electrolytic quadrivalent platinum derivatives are prepared and described: *triamminonitrodichloroplatinum chloride,* $[(NH_3)_3\ NO_2\ Cl_2\ Pt]Cl$, *triamminodinitrochloroplatinum chloride,* $[(NH_3)_3\ (NO_2)_2\ Cl\ Pt]Cl$, *diamminopyridinonitrodichloroplatinum chloride,* $[C_5H_5N\ NH_3\ NO_2\ NH_3\ Cl\ Pt]Cl$, optically active *diamminopyridinodinitrochloroplatinum chloride,* $[C_5H_5N\ NH_3\ NO_2\ NH_3\ NO_2\ Cl\ Pt]Cl$, *amminopyridinomethylaminonitrodichloroplatinumammine chloride,* $[C_5H_5N\ NH_3\ NH_2Me\ NO_2\ Cl_2\ Pt]Cl$, optically active *amminopyridinomethylaminodinitrochloroplatinum chloride,* $[C_5H_5N\ NH_3\ NH_2Me\ NO_2\ NO_2\ Cl\ Pt]Cl$, *ethylenediaminopyridinonitrodichloroplatinum chloride,* $[en\ C_5H_5N\ NO_2\ Cl_2\ Pt]Cl$, its dextrorotatory *stereoisomeride,* $[en\ C_5H_5N\ Cl\ NO_2\ Cl\ Pt]Cl,2H_2O$, d-*ethylenediaminopyridinodinitrochloroplatinum chloride,* $[en\ C_5H_5N\ NO_2\ Cl\ NO_2\ Pt]Cl,2H_2O$, *ethylenediaminopyridinotrichloroplatinum chloride,* $[en\ C_5H_5N\ Cl_3\ Pt]Cl$, *amminoethylenediaminonitrodichloroplatinum chloride,* $[en\ NO_2\ NH_3\ Cl_2\ Pt]Cl$, its d- and l-*isomerides,* $[en\ NH_3\ Cl\ NO_2\ Cl\ Pt]Cl$ and $[en\ NO_2\ Cl\ NH_3\ Cl\ Pt]Cl,H_2O$, *amminoethylenediaminotrichloroplatinum chloride,* $[en\ NH_3\ Cl_3\ Pt]Cl$, *tetramminonitrochloroplatinum chloride,* $[(NH_3)_2\ NO_2\ NH_3\ Cl\ NH_3\ Pt]Cl_2$, optically active *triamminopyridinonitrochloroplatinum chloride,* $[NH_3\ C_5H_5N\ NH_3\ NO_2\ NH_3\ Cl\ Pt]Cl_2,H_2O$, l-*diamminoethylenediaminodichloroplatinum chloride,* $[en\ NH_3\ Cl\ NH_3\ Cl\ Pt]Cl$, l-*diamminoethylenediaminonitrochloroplatinum chloride,* $[en\ NH_3\ NO_2\ NH_3\ Cl\ Pt]Cl_2$, optically active *amminoethylenediaminopyridinodichloroplatinum chloride,* $[en\ C_5H_5N\ Cl\ NH_3\ Cl\ Pt]Cl_2,H_2O$, and optically active *amminoethylenediaminopyridinonitrochloroplatinum chloride,* $[en\ C_5H_5N\ NO_2\ NH_3\ Cl\ Pt]Cl$.

(I.) 

 (II.)

R. Truszkowski.

Thiocyanates of bivalent platinum. A. A. Grünberg (Ann. Inst. Platine, 1928, 6, 122—177).—The following compounds are prepared and described: cis- and trans-*dithiocyanoplatinumdiammine,*  $\begin{matrix}SCN\\SCN\end{matrix}>Pt<\begin{matrix}NH_3\\NH_3\end{matrix}$ and  $\begin{matrix}SCN\\NH_3\end{matrix}>Pt<\begin{matrix}NH_3\\SCN\end{matrix}$, cis- and trans-*dipyridinodithiocyanoplatinum,* and *ethylenediamminodithiocyanoplatinum.* Ammonia and amines react with potassium thiocyanoplatinite to yield analogues of Peyronne's salt, possessing the *cis*-configuration. Complexes of the above type react with thiocarbamide according to Kurnakov's rules. Jergensen's rule, whereby tetrammine bases should yield *trans*-derivatives on heating, is not followed by thiocyano-salts. *cis*-Dithiocyanoplatinumdiammine is less stable than the *trans*-isomeride, although direct transformation of the less to the more stable form was not observed. The stabilising influence of the ethylenediamine ring on bases of the above type is shown also by the thiocyano-derivatives. Potassium chloroplatinite reacts with potassium thiocyanoplatinite to form platinous thiocyanate and potassium chloride. *cis*-Dithiocyanoplatinumdiammine combines with silver nitrate to yield  $\left[\begin{matrix}NH_3\\NH_3\end{matrix}>Pt<\begin{matrix}SCN\\SCNAg\end{matrix}\right]NO_3$, the *trans*-isomeride yielding a more complex product. Peyronne's rule is explained on the assumption that salts of the type PtX_2 have the *cis*-configuration. Measurements of the mol. wt. of the above isomerides of the type $PtA_2(SCN)_2$, dissolved in acetone, show that these bases are isomerides and not polymerides, as found in liquid ammonia solution by Reihlen and Nestle (cf. A., 1926, 699). In bromoform, *cis*-dipyridinodithiocyanoplatinum exhibits association not found for the *trans*-isomeride.

R. Truszkowski.

[Ruthenium chlorides.] H. Gall and G. Lehmann (Ber., 1928, **61**, [*B*], 1573—1576).—A reply to Remy and Lührs (this vol., 722). It is shown that the product obtained by the action of hydrochloric acid on ruthenium tetroxide is not an individual, but corresponds analytically with a mixture of ruthenium tri- and tetra-chlorides. The green colour of ruthenium chloride solution has been attributed by Remy to the tervalent metal. Since, however, such solutions of the metal are brown, the supposition involves the assumption of isomeric ruthenium trichlorides, which does not appear justified. The colour is attributed by the authors to the mixture of brown and blue. H. WREN.

Stability of rhodium sesquioxide and of iridium dioxide. S. PASTORELLO (Atti R. Accad. Lincei, 1928, [vi], 7, 754—757).—The behaviour of the above oxides in a current of sulphur dioxide at temperatures above 350° has been examined by *X*-ray methods. The oxide of rhodium is stable up to 450° but is reduced to the metal above this temperature. Iridium dioxide is stable up to 650°. The results support the view that the decreased activity of platinum containing rhodium or iridium in the catalytic oxidation of sulphur dioxide to sulphur trioxide is due to the formation of rhodium sesquioxide and iridium dioxide, respectively (cf. Levi and Faldini, B., 1927, 651). O. J. WALKER.

Distillation of osmium tetroxide in aqueous solution, and oxidation of osmium and its compounds. E. FRITZMANN (Ann. Inst. Platine, 1928, **6**, 101—115).—See A., 1927, 742. R. TRUSZKOWSKI.

Magnitude of observation errors in chemical analysis. A. E. KORVEZEE and N. H. J. M. VOOGD (Chem. Weekblad, 1928, **25**, 242—247; cf. Goudriaan, this vol., 262; Hartong, *ibid.*, 382).—A mathematical analysis of the probability and effect of errors of observation. S. I. LEVY.

Natural classification of the elements and the qualitative analysis grouping. J. GILLIS (Natuurwetensch. Tijds., 1928, **10**, 47—52).—The arrangement of the elements in the form proposed by Antropoff (A., 1926, 773) may be employed to throw up the division usually adopted in analytical work into groups based on the solubilities of the sulphides and carbonates. S. I. LEVY.

Quantitative analysis depending on change in density. A. SHESTKOV (J. Chem. Ind. [Russia], 1927, **4**, 762—763; Chem. Zentr., 1928, i, 1306).—The quantity of solid precipitated or gas evolved in a reaction is determined by measurement of the density change of the solutions. The method can be applied to oxidation reactions by precipitation of an ionic product of the reaction. A. A. ELDRIDGE.

Electronic interpretation of oxidation and reduction in analytical chemistry. L. DUPARC, E. ROGOVINE, and P. WENGER (Helv. Chim. Acta, 1928, **11**, 577—583).—Oxidation is regarded as an increase in positive valency of the substance oxidised and a decrease in positive valency of the oxidising agent, the former signifying a loss and the latter a fixing of electrons. The reduction of potassium permanganate and dichromate, and the oxidation of ferrous iron, oxalic acid, alcohol, and potassium iodide are discussed on these lines, together with the more complex case of arsenious sulphide and nitric acid. L. S. THEOBALD.

Reduction of the weight of powdered substances weighed in air to that in a vacuum. R. RUER and J. KUSCHMANN (Z. anorg. Chem., 1928, **173**, 233—261; cf. A., 1927, 1134).—Neither calcium chloride nor sodium nitrate adsorbs air on the surface. Finely-divided silver, copper, and iron reduced from their oxides at 750° have no adsorptive power for air, but silver and iron adsorb 5 mg./100 g. of carbon dioxide. Exposure to pure dry air, however, results in slight oxidation, 100 g. of iron increasing in weight 30 mg., 100 g. of copper 10 mg., and 100 g. of silver 4 mg. Oxidation of filings of iron and copper also takes place in dry air but not nearly to the same extent as with the powders. For exact chemical work, *e.g.*, the determination of at. wts., no measurable error is introduced by omitting to take into account this slight oxidation. A. R. POWELL.

Analytical application of iodine trichloride to oxidation and of sodium formate to reduction. E. BIRK (Z. angew. Chem., 1928, **41**, 751).—A 20% solution of iodine trichloride in concentrated hydrochloric acid may be used for analytical oxidations, *e.g.*, of finely-divided sulphur in solutions. Fusion with sodium formate and consequent reduction is recommended as a means of solubilising certain insoluble substances; *e.g.*, anhydrous chromic chloride is thus converted into a soluble mixture of chromium formate and chloride. Fusion of a tungsten ore with sodium formate and lithium carbonate yields a characteristic deep blue lithium tungsten bronze. A. DAVIDSON.

Apparatus for continuous gas analysis. E. C. WHITE (J. Amer. Chem. Soc., 1928, **50**, 2148—2154).—An apparatus which affords a continuous determination of moderate concentrations of a given constituent in a flowing gas mixture, and registers the concentration automatically by electrical means, is described. A definite proportion of gas is scrubbed with a suitable absorbent, the titre of the resulting solution being determined by conductivity measurements. The method may be used for the determination of ammonia, hydrogen chloride, sulphur dioxide, chlorine, hydrogen sulphide, and carbon dioxide, and also may be adapted to the determination of carbon monoxide in presence of hydrogen and hydrocarbons. S. K. TWEEDY.

Microscopical examination of metallic minerals. J. ORCEL (Bull. Soc. d'Encour., 1928, **127**, 503—527).—A description of the technique of the preparation, etching, and microscopical examination of sections of minerals. C. W. GIBBY.

Spectrophotometric determination of hydrogen-ion concentrations and of the apparent dissociation constants of indicators. V. Fast-green FCF ["*p*-hydroxyerioglucine *A*"]. W. C. HOLMES and E. F. SNYDER (J. Amer. Chem. Soc., 1928, **50**, 1907—1910).—Data are supplied for the determination of hydrogen-ion concentrations at p_H 6·7—10·0 with the aid of fast-green FCF. The apparent dissociation constant of the dye in this range is approximately 8·1(5) at 29° (cf. A., 1925, ii, 999). S. K. TWEEDY.

Apparatus for potentiometric titration. E. LINDE (Svensk Kem. Tidskr., 1927, **39**, 285—287; Chem. Zentr., 1928, i, 725—726).—A method depending on the use of a triode valve is described. A. A. ELDRIDGE.

Potentiometric micro-titrations. E. Zintl and K. Betz (Z. anal. Chem., 1928, **74**, 330—342).—It is shown mathematically that the potentiometric end-point of a process involving precipitation is premature by an amount Δ c.c., such that $\Delta=8Lv/N^2$, where L is the solubility product involved, v the volume of the solution, and N the normality of the titrating solution. The value of Δ is usually negligible under ordinary conditions, but is often not inconsiderable in micro-determinations. It is possible, however, using a silvered platinum wire as indicator electrode, to titrate chlorides and bromides with 0·001N-silver nitrate and iodides with 0·0001N-silver nitrate without involving any serious error. The volume of the solution should, however, be kept small. Potentiometric micro-titration of mixtures of two halides is possible, but titrations of solutions containing all three halides yield untrustworthy results. Contrary to the statement of Mislowitzer and Vogt (A., 1925, i, 1485), it is possible to determine chloride in presence of serum potentiometrically.

When the amount of arsenic is less than 0·1 mg. the indicator correction is such that the visual titration with potassium bromate yields untrustworthy results. When the volume of the solution is kept small, *e.g.*, 5—10 c.c., amounts of arsenic of this order may be determined with considerable accuracy by the potentiometric method, using 0·001N-potassium bromate. The titrated solution should contain 10% of hydrochloric acid. Smaller quantities of arsenic, *e.g.*, 0·002 mg., may be determined using 0·0001N-bromate. The observed values are, however, about 8% too high. Quantities of arsenic of the order 0·1 mg. may be determined with accuracy in presence of considerable quantities of copper salts.

J. S. Carter.

Hydrogen-ion concentration measurements. I. Methods of measurements. C. E. Davis and G. M. Davidson (J. Amer. Chem. Soc., 1928, **50**, 2053—2065).—The inherent errors of the electrometric method of determining hydrogen-ion concentrations with a condenser apparatus are investigated (cf. Beans and Oakes, A., 1921, ii, 12). The method is useless for precise work; errors due to humidity, the galvanometer throw, and the method of calculation arise. A mathematical discussion of the important errors is given, and their significance illustrated by graphs representing the titration of sulphuric and orthophosphoric acids by 0·1N-sodium hydroxide. The accumulated errors may attain ±4 millivolts.

S. K. Tweedy.

Differential potentiometric titration. N. F. Hall, M. A. Jensen, and S. A. Baeckström (J. Amer. Chem. Soc., 1928, **50**, 2217).—The glass isolation vessel in MacInnes and Jones' method of differential potentiometric titration (A., 1927, 35) may be replaced by a fountain-pen filler having a small side arm near the bulb. One wire is wrapped round the filler, whilst the other passes into the interior through the side arm, which is then sealed.

S. K. Tweedy.

Volumetric determination of acids and bases in various solvents. K. Linderstrøm-Lang (Dansk Tidsskr. Farm., 1928, **2**, 201—232).—A theoretical paper on the errors involved in the titration of acids and bases, Brønsted's views (Rec. trav. chim., 1923, **42**, 718) regarding the nature of these substances being adopted. The errors of titration can frequently be greatly reduced by carrying out the operation in a non-aqueous medium. Thus in the titration of glycine with hydrochloric acid the error may amount to as much as 5% if the determination is carried out in aqueous solution, but this can be reduced to 0·4% by employing 90% ethyl alcohol as solvent. Most amino-acids can also be determined practically quantitatively by titration with hydrochloric acid if they are dissolved in 90—95% acetone, naphthol-red being used as indicator.

H. F. Harwood.

Indicators. XII. Azo-indicators. A. Thiel and O. Peter (Z. anorg. Chem., 1928, **173**, 169—198).—Methyl-orange exists as a yellow, purely azo-form and as a red, practically completely quinonoid, form. The electrochemical and colour equilibria coincide almost exactly, the indicator thus satisfying the modified Ostwald theory of indicators. The double change is limited to the *p*-aminoazobenzene-*o*-carboxylic acid derivatives. Considerable evidence has been obtained for the hypothesis of closed ring formation. A number of relationships exist between the indicator properties of a substance and its constitution. The half-way stages of all sulphonic and *m'*- and *p'*-carboxylic acids are practically identical and are in accord with those of the free bases having similar amino-complexes. The *o'*-carboxylic acids are bivalent indicators, of which the half stage of the first change (basic) lies below that of substances of the first group having the same amino-complexes. The colour change of the yellow forms of the acidic indicators increases in the order *o'*-, *m'*-, *p'*-, whilst for the red forms the order is *o'*-, *m'*-, *p'*- for the sulphonic acids and *m'*-, *p'*-, *o'*- for the carboxylic acids, successive increases being produced in all cases by substitution in the amino-group in the order: unsubstituted, dimethyl and monophenyl, diethyl, for the yellow forms, and unsubstituted, diethyl, dimethyl, monophenyl for the red forms. The depth of colour of all the indicators increases by substitution in the amino-group in the order unsubstituted, monophenyl, dimethyl, diethyl for the yellow forms and unsubstituted, dimethyl or diethyl, monophenyl for the red forms.

H. F. Gillbe.

Electrometric determination of hydrogen peroxide and the associated peracids. A. Rius (Trans. Amer. Electrochem. Soc., Sept. 1928, advance copy, 15—28).—In a solution containing hydrogen peroxide, permonosulphuric acid, and perdisulphuric acid the three constituents may be determined as follows: The permono-acid is determined by electrometric titration with sodium sulphite solution (containing 5% of 96% alcohol, which renders the solution more stable to atmospheric oxidation). As indicator electrode a strip of platinum 2×2·5 cm. is used, and the sample to be titrated is diluted to 200 c.c. with 2N-sulphuric acid. This method is also satisfactory for the determination of permonophosphoric acid. Electrometric titration of permonosulphuric acid by means of ferrous sulphate in presence of manganous sulphate is accurate only in the absence of hydrogen peroxide. The presence of much perdisulphuric acid interferes. Hydrogen peroxide in presence of the persulphuric acids is determined by a modification of Birkenbach's method of titration with potassium permanganate, the latter being added rapidly to the peroxide solution. By determination of the total oxidising value of the solution and subtraction of the equivalents of hydrogen peroxide and permonosulphuric acid as determined above the amount of perdisulphuric acid may be determined. The *E.M.F.* change in a *N*-calomel Pt,H_2SO_5 cell on addition of small amounts of hydrogen peroxide forms a sensitive method for the detection of the peroxide.

O. J. WALKER.

Microchemical reactions of the acids of chlorine, bromine, and iodine. E. M. CHAMOT and C. W. MASON (Mikrochem., 1928, **6**, 82—91).—A characteristic test for periodates in neutral solution is the formation, on addition of silver nitrate, of a fine-grained yellow to orange precipitate which becomes nearly black when heated and consists of small hexagonal prisms and triangular plates; as confirmatory tests the precipitation of the potassium salt and the starch test after reduction are recommended. Iodates are distinguished from periodates by the formation of a precipitate with barium chloride. Perchlorates are distinguished by their reaction with potassium salts and by the formation of thin rectangular crystals with strychnine sulphate. Chlorates should be reduced to chlorides for testing and bromates are distinguished in the presence of chlorates by the *m*-phenylenediamine test. Numerous other well-known tests for these and other halogen acids are also useful for microchemical work.

A. R. POWELL.

Determination of small quantities of free chlorine. K. ALFTHAN (Finska Kemistamfundets Medd., 1927, **36**, 109—112; Chem. Zentr., 1928, i, 1306—1307).—*as*-Dimethyl-*p*-phenylenediamine hydrochloride (1 c.c. of 0·1% solution) is added to the acidified tap water (100 c.c.) and the colour compared with a standard solution of methyl-red.

A. A. ELDRIDGE.

Iodometric determination of ozone and chlorine. A. JULIARD and S. SILBERSCHATZ (Bull. Soc. chim. Belg., 1928, **37**, 205—224).—The use of neutral or alkaline solutions of potassium iodide for the determination of ozone is attended by considerable error. Trustworthy results are obtained only by keeping the iodide solution at a hydrogen-ion concentration of p_H 7 by means of a suitable buffer mixture, or by making acid with an excess of boric acid. Since the presence of the buffer mixtures interferes in no way with the determination of chlorine by potassium iodide, such solutions may be used for the analysis of mixtures of chlorine and ozone.

F. J. WILKINS.

Detection of minute traces of iodine. A. N. SCHUKAREV and SYSOEV (J. Russ. Phys. Chem. Soc., 1928, **60**, 669—671).—On placing a small electrolytic cell provided with a very sensitive galvanometer in an electromagnetic field, a minute current is induced in the cell circuit. 0·1*N*-Potassium iodide, potassium chloride, or sodium chloride solutions gave *E.M.F.* of about $3{\cdot}8\times10^{-6}$ volt. On addition of traces of iodine (8×10^{-5}%) the *E.M.F.* is increased threefold. The phenomenon is due to depolarisation by the iodine of the electrodes, with a consequent increase in the current. The method is shown to be sensitive to 3×10^{-5}% of iodine.

M. ZVEGINTZOV.

Detection of sulphur and sulphurous acid. A. NOLL.—See B., 1928, 567.

Quantitative precipitations in concentrated solutions. V. NJEGOVAN and V. MARJANOVIĆ (Z. anal. Chem., 1928, **74**, 191).—In the method previously described 1 c.c. of saturated barium chloride solution is added for every 0·125 g. of sulphate ion present (cf. this vol., 497).

A. R. POWELL.

Determination of sulphur trioxide in natural waters and soil extracts. B. G. ZAPROMETOV (Bull. Univ. Asie. Centr., 1927, 91—95).—Raschig's benzidine method (A., 1903, ii, 572, 691) is preferred; the filtration with suction of the benzidine sulphate is omitted.

CHEMICAL ABSTRACTS.

Stable sodium thiosulphate solution. L. W. WINKLER.—See B., 1928, 567.

Determination of active oxygen in a mixture of persulphuric acid and hydrogen peroxide. G. D. LUBARSKI and M. G. DIKOVA (J. Russ. Phys. Chem. Soc., 1928, **60**, 735—741).—Le Blanc and Eckhardt's method (A., 1900, ii, 45) for the determination of active peroxide and persulphate oxygen gives low results, probably as a result of formation of molecular oxygen. Ferber's method (Diss., Dresden, 1913) gives high results, owing to the catalytic action of ferric salts, which liberate iodine from iodides even in the absence of active oxygen. Wolffenstein and Makow's method (A., 1923, ii, 652) also gives low results. The only method which gives results comparable with those obtained by gasometric analysis is the following. Five c.c. of the solution under examination are left in a flask with 150 c.c. of water and 5 c.c. of 10% potassium iodide for 24 hrs. below 20°, and shielded from direct sunlight, after which iodine is determined volumetrically.

R. TRUSZKOWSKI.

Sources of error in organic micro-elementary analysis. I. Determination of nitrogen by Dumas' method. F. BÖCK and K. BEAUCOURT (Mikrochem., 1928, **6**, 69—81).—The occasional slightly high results obtained in Pregl's microchemical method of determining nitrogen are attributed to incomplete removal of adsorbed gases in the copper oxide packing in the tube by a cold current of carbon dioxide. This source of error is avoided by carrying out a blank analysis at the beginning of a series of tests and using the same coarse copper oxide for a number of tests, changing only the fine copper oxide with every test. There is no advantage in arranging the copper column at the end of the tube as recommended by Dubsky, for Pregl's original arrangement of this column between two columns of copper oxide is equally satisfactory.

A. R. POWELL.

Modified digestion acid for non-protein nitrogen determination. M. DUPRAY (J. Lab. Clin. Med. 1927, **12**, 387).—A mixture of sulphuric, perchloric, and phosphoric acids is employed, so that no precipitate is formed. Chemical Abstracts.

Determination of nitrates. II. L. Szebellédy (Z. anal. Chem., 1928, 74, 232—235).—Arsenates, sodium, ammonium, magnesium, calcium, strontium, aluminium, manganous, zinc, antimony, silver, or cadmium salts do not interfere with the determination of nitrate by the author's method (this vol., 498). In presence of lead, mercuric, bismuth, and often barium salts the end-point is somewhat obscured by the white precipitate formed and a comparison solution is advisable. In presence of copper and nickel the colour changes are from yellowish-green to blue and green, respectively, and the use of a comparison solution is essential. Determinations are impossible in presence of cobalt and chromium salts and determinations in presence of mercurous salts are not entirely satisfactory. In absence of free arsenic, arsenious oxide does not interfere. J. S. Carter.

Determination of nitrites in soil. R. P. Bartholomew.—See B., 1928, 538.

Ciurea's modification of Denigès' method for the micro-determination of phosphorus. I. Voicu (Bul. Soc. Chim. România, 1928, **10**, 50—54).—Polemical against Ciurea (this vol., 384). It is alleged that there is no proportionality between the amount of phosphorus and the amount of chlorine water used to destroy the blue colour. Decolorisation is never complete. J. S. Carter.

Indicator for volumetric determination of phosphoric acid. L. Duparc and E. Rogovine (Helv. Chim. Acta, 1928, **11**, 598—599).—The intense orange coloration produced by adding uranyl acetate to an aqueous solution of sodium salicylate is used for the determination of phosphoric acid. To 20 c.c. of the solution to be analysed, and 20 c.c. of a standard solution of 5·46 g. of calcium phosphate dissolved in nitric acid and diluted to 1 litre, are added 50 c.c. of water and 10 c.c. of a 10% aqueous solution of sodium salicylate. The solutions are heated to boiling and the uranyl acetate (13—15 g./litre) solution is added to each until an orange-yellow colour is obtained. The colours are matched either in the presence of the heavy precipitates which form during titration or in the clear liquids. Centrifuging can be employed, but is not essential. The method can be applied to the determination of phosphoric acid in urine when the latter is diluted six times with water to reduce the depth of colour. The standard solution is similarly diluted in this case. L. S. Theobald.

Microchemical determination of phosphoric acid as strychnine phosphomolybdate. C. Antoniani and R. B. Jona (Giorn. Chim. Ind. Appl., 1928, **10**, 203—205).—Modifications of Embden's method (A., 1921, ii, 462) are found advisable. The time of sedimentation of the precipitate is without effect, provided that it is at least 30—40 min., and the precipitation is not impaired by excess of the strychnine–molybdic acid reagent, but 6 parts of strychnine to 1 part of P_2O_5 represent the best conditions. Excess either of nitric acid beyond that of the reagent or of other free acid is harmful, but salts of organic acids, extraneous inorganic salts, and silicic acid are without influence; arsenic acid behaves like phosphoric acid. The results obtained are more constant if the precipitate is washed with 10% nitric acid solution instead of with the fivefold diluted reagent, and the method is applicable to quantities of P_2O_5 ranging from 1 to 6·3 mg. Good results are obtained with nitric–hydrochloric acid extracts of soil or mineral superphosphate and with sulphuric acid solutions of Thomas slag, the acid solutions being neutralised with sodium hydroxide solution and then re-acidified with nitric acid to dissolve the separated hydroxides, prior to precipitation of the phosphate with the strychnine–molybdic acid reagent. T. H. Pope.

Titration of phosphoric and boric acids present in the same solution by the citrate method. W. M. Deerns (Chem. Weekblad, 1928, **25**, 268—271).—The end-points are not sharp, and the colour change interval is influenced, not only by the quantities of the various materials present, but also by the concentration of the indicator itself. The chemistry of the changes is very complicated, and equilibrium is attained in some cases only after considerable intervals. S. I. Levy.

Apparatus for micro-determination of carbon dioxide. L. Lescœur (J. Pharm. Chim., 1928, [viii], 8, 11—18).—An apparatus for circulating a gas in a closed circuit over a suitable absorption reagent is described. The circulation of the gas is effected by a small mercury pump, consisting of a reservoir of mercury which is allowed to empty itself slowly through the atmosphere of carbon dioxide formed by the action of hydrochloric acid on the test solution. The drops of mercury falling through a tube of calculated diameter aspirate the gas over their upper surface while compressing it on the lower surface, thus behaving as a series of pistons. Generally not more than 25 min. are required for the complete absorption of carbon dioxide. R. A. Pratt.

Determination of alkalis in sub-soil waters. K. L. Maliarov (J. Russ. Phys. Chem. Soc., 1928, **60**, 829—834).—The alkali metal content of sub-soil water is determined, after precipitating sulphates with barium and elimination of chlorides by heating to dryness with excess of oxalic acid, by converting the remaining oxalates into carbonates, the quantity of which is determined by titration with standard acid. R. Truszkowski.

Use of dihydroxytartaric acid for the detection and determination of sodium. A. P. Okatov (J. Russ. Phys. Chem. Soc., 1928, **60**, 661—668).—Dihydroxytartaric acid was obtained in 90% yield by Fenton's method of oxidising dihydroxymaleic acid with bromine in glacial acetic acid solution. The solubility of the sodium salt was determined at 0° (0·032%) and 10° (0·053%) by titrating the solution with potassium permanganate. A solution of the potassium salt is a qualitative reagent for sodium up to 0·05*N*-concentration at 12·5° and 0·025*N* at 0°. The solution, however, decomposes in a few days. It can be used for the determination of sodium, provided the determination is carried out at 0°, and a correction introduced for the solubility of the sodium salt. M. Zvegintzov.

Influence of impurities from glass on the titre of sodium hydroxide. W. Böttger (Schweiz. Apoth. Ztg., 1927, 65, 549—553; Chem. Zentr., 1928, i, 726).—Ampoules which had contained 5*N*-sodium hydroxide solution for 3 yrs. showed a change of more than 1—1·8% only when dimethyl-yellow was used as indicator. A. A. Eldridge.

Apparatus for titration with carbonate-free sodium hydroxide. H. W. van Urk (Pharm. Weekblad, 1928, 65, 390).—The burette is provided with a lower side-arm and tap, by means of which the solution is measured out. Below the ordinary bottom tap the burette is prolonged into a capillary which dips below the surface of the solution contained in a Woulf's bottle, the joint being air-tight. The second neck of the bottle is closed by a cork bearing a soda-lime tube, through which, by means of a pump, pressure can be exerted to refill the burette, which is also provided with a soda-lime tube at the top. S. I. Levy.

Volumetric determination of potassium. G. Jander and O. Pfundt (Chem. Fabr., 1928, 435—436, 446—448).—An account of work already published (A., 1927, 1046), with a description of modified apparatus.

Rapid gasometric determination of potassium. G. Jander and H. Faber (Z. anorg. Chem., 1928, 173, 225—232).—The difficulties in employing sodium cobaltinitrite as a quantitative reagent for potassium are discussed. In order to obtain a precipitate having a constant sodium : potassium ratio it is necessary to work with solutions saturated with sodium chloride and to stir vigorously during the formation of the precipitate. By treating the washed precipitate with a concentrated solution of ferrous sulphate in 2*N*-sulphuric acid, potassium may be rapidly determined by measuring the volume of nitric oxide evolved. H. F. Gillbe.

Microchemical detection of silver as sulphate. O. Hackl (Mikrochem., 1928, 6, 106—107).—The characteristic rhombic crystals of silver sulphate serve for the microchemical detection of silver in concentrations exceeding 2 mg. per c.c. if 1 drop of the solution is evaporated with 1 drop of 2% sulphuric acid. A. R. Powell.

Potentiometric analysis. II. Determination of silver and the halogens. T. Heczko (Z. anal. Chem., 1928, 74, 289—308; cf. this vol., 726).—The principle of the method is the same as that previously described for the potentiometric determination of iron with permanganate, but for argentometric work a silver indicator electrode is used and the absorbent electrode consists of a thin rod of pine-wood. The end-point may be determined either by measuring the throw of the galvanometer needle for every addition of solution or by measuring the strength of the residual current after each addition. For the determination of chloride, bromide, iodide, or silver, 5% of ammonium nitrate is added to the liquid to be titrated to increase the conductivity, and for the determination of two halogens consecutively in the same solution 6% of barium nitrate is added to render the two maxima more pronounced and to reduce errors due to adsorption by the first silver salt precipitated. A. R. Powell.

Microchemical determination of calcium. F. Rogozinski (Bull. Soc. chim., 1928, [iv], 43, 464—469).—A microchemical method for the determination of calcium (*e.g.*, 0·27—1·1 mg.) by precipitation with sulphuric acid in presence of alcohol is described. After 12—21 hrs. the supernatant liquid is removed; the precipitate, $CaSO_4,2H_2O$, is filtered through a Pregl filter, washed with 96% alcohol, and dried at 105° in a current of filtered air. The presence of moderate amounts of hydrochloric acid or magnesium salts has no influence on the accuracy of the process. W. A. Richardson.

Use of oxalic acid in microchemical analysis. K. L. Maljarov (Mikrochem., 1928, 6, 92—96).—The property of oxalic acid of expelling volatile acids from their salts affords a useful method of separating alkalis from alkaline earths and both these groups from the heavy metals. Thus, if a chloride or nitrate solution is evaporated with an excess of oxalic acid and the residue is heated until the excess is expelled, the alkaline earths are converted into insoluble carbonates and the alkalis into soluble carbonates. To separate alkaline earths from magnesia the oxalate residue is ignited to obtain the oxides, from which the alkaline earths may be extracted with water free from carbon dioxide. Zinc, copper, and manganese are dissolved from admixture with iron and aluminium by extracting the ignited oxalate residue with dilute hydrochloric acid. Chromium and manganese solutions are freed from chlorides by evaporation with oxalic acid and ignition of the residue. A. R. Powell.

Rapid determination of magnesium. L. Galimberti and E. Zoccheddu (Annali Chim. Appl., 1928, 18, 286—288).—Either in presence or in absence of alkali chlorides or sulphates, magnesium may be determined alkalimetrically, the results obtained agreeing closely with those furnished by gravimetric determinations. An excess of 0·1*N*-sodium hydroxide solution is run from a burette into a 250 c.c. flask containing a definite volume of the solution together with methyl-orange, practically complete precipitation of magnesium hydroxide being thus effected. The liquid is diluted to 250 c.c. with water, shaken vigorously, left for some minutes, and filtered rapidly through a hard, pleated filter, 100 c.c. of the filtrate being carefully titrated with 0·1*N*-hydrochloric acid in presence of methyl-orange until the yellow colour just begins to change to orange; addition of a few drops of phenolphthalein to the liquid facilitates the titration, as this indicator becomes colourless just before the change of the methyl-orange. The difference between the volume of alkali first used and that of the acid ultimately required for neutralisation corresponds with the magnesium present in accordance with the equation, $2NaOH+MgCl_2=NaCl+Mg(OH)_2$. T. H. Pope.

Electro-analytical determination of lead. A. V. Pamfilov and A. A. Blagonravona (J. Russ. Phys. Chem. Soc., 1928, 60, 699—706).—Various electro-analytical methods of determining lead are discussed, and their accuracy is compared with gravimetric and volumetric methods. Deposition of lead as the peroxide at the anode, with subsequent weighing of the deposit, gives inaccurate results, but this can be avoided if the peroxide is reduced by heat to the monoxide. For cathodic deposition in hydrochloric acid solution various depolarisers, such as gallic acid and hydroxylamine hydrochloride, have been tried with moderate success. The deposits, however, are generally spongy and corrode the platinum cathodes. Coating the latter with copper and the use of mercury amalgams is not very successful. Further, it is almost impossible to avoid some lead peroxide deposition on the anode, consequently the cathode deposition method is greatly inferior in accuracy to the anode method.

M. Zvegintzov.

Toxicology of lead and its compounds. IV. Electrolytic detection of lead. V. Nephelometric determination of lead. P. W. Danckwortt and E. Jurgens (Arch. Pharm., 1928, **266**, 367—374, 374—382).—IV. Methods of detecting lead by colour reactions with organic compounds (cf. A., 1923, ii, 508; 1925, ii, 1095; 1927, 277) were unsuccessful when used with animal organs or foodstuffs and the " triple-nitrite test " (A., 1922, ii, 659; 1924, ii, 61) had also to be abandoned. The accurate chromate method (Arch. Pharm., 1927, **265**, 424) is troublesome and the following simple electrolytic method was adopted. On a glass slide with hollowed part 0·5 cm. in diameter were fixed two platinum wires with ends 5 mm. apart and placed so that no liquid could rise between the sides of the hollow part and the wires. A current of 2·4 amp. at 4 volts was employed and the separation of metallic lead in tree-form noted at the cathode under the microscope, whilst lead dioxide deposited at the anode. The latter when mixed with tetramethyl-*p*-diaminodiphenylmethane (cf. A., 1902, ii, 352) developed a blue colour at the edges. To study the behaviour of other metals, especially those occurring with lead, 0·2*N*-solutions of lead, bismuth, mercury, iron, copper, manganese, and cadmium nitrates were electrolysed under the same conditions, using 3 drops of the solution. The metals all behave characteristically, manganese and lead alone being deposited as dioxides, which gave a blue colour with the above base. The results of electrolysis in nitric acid solution and with the addition of phosphoric acid are also described. The solutions examined contained 1 mg. of metal per 1 c.c. Phosphoric acid may be used to give only cathodic deposition with lead, and 0·010 mg. of lead can be detected. By anodic deposition 0·003 mg. of lead can be detected by the colour method. Since the presence and separation of other metals during electrolysis hinders the detection of lead, their influence on the cathodic and anodic deposition of the latter metal is described from the results of electrolysis of lead nitrate along with those of the above metals in turn, in neutral, nitric and phosphoric acid solutions. Lead in each case can be detected, and in acid solution manganese was easily recognised by conversion into permanganate. As iron and copper occur most often in biological material with lead, different mixtures of these metals were electrolysed, and whilst cathodic deposition is of no value, yet lead can be detected by the colour reaction in quantities of 0·005 mg. per drop in presence of ten times this amount of copper and iron. The detection of lead can be made in each case directly after destruction of organic material in the nitric acid solution.

V. The colour reaction of lead salts with hæmatin (A., 1907, ii, 653) is affected by the presence of copper and zinc, and whilst the colorimetric method with Arnold's reagent (A., 1902, ii, 352) is delicate the apparatus is expensive, so the nephelometric method (cf. A., 1907, ii, 398) was applied to the toxicological determination of lead, using Kleinmann's apparatus (A., 1925, i, 473). Optically clear 1% potassium dichromate solution (5 c.c.) is mixed with 5 drops of acetic acid. The lead solution (1 c.c. containing 0·0558 mg. of lead) is added and allowed to react for 20 min.; the volume is then made up to 20 c.c. with distilled water. Nephelometric readings can be taken between 10 and 60 min. after mixing; consistent results are obtained when the conditions are standardised. Favourable results were also obtained by diluting a mixture of 10 c.c. of 1% potassium dichromate solution, 15 drops of acetic acid, and 2 c.c. of the above lead solution. The presence of sodium or copper acetate has no effect, but copper nitrate may not be present. Except in acid solution the presence of iron gives rise to inaccuracy (A., 1908, ii, 633). By the above method 0·006 mg. of lead can be determined.

J. D. Fulton.

Volumetric determination of mercury. L. Maricq (Bull. Soc. chim. Belg., 1928, **37**, 241—251).—The only satisfactory method of determining mercury in concentrations of 0·1—0·001*N* is an electrometric modification of the Personne–Denigès method, in which the mercury salt is titrated against potassium iodide. The results are accurate to within 1% even in presence of relatively large amounts of nitric and sulphuric acids, and chlorides, acetates, and phosphates.

F. J. Wilkins.

Rapid separation of aluminium and beryllium. I. M. Kolthoff and E. B. Sandell (J. Amer. Chem. Soc., 1928, **50**, 1900—1904).—From a slightly acid solution containing aluminium and beryllium the former is quantitatively precipitated as $Al(C_9H_6ON)_3$ by the addition of an acetic acid solution of 8-hydroxyquinoline (" oxine ") and an excess of ammonium acetate, the precipitate being weighed after drying at 120—140°. Beryllium hydroxide is precipitated from the filtrate by the addition of ammonia solution and ignited to the oxide. The method may also be used to separate beryllium from ferric iron.

S. K. Tweedy.

Gallium. III. Quantitative separation of [ferric] iron from gallium by means of 1-nitroso-β-naphthol. J. Papish and L. E. Hoag (J. Amer. Chem. Soc., 1928, **50**, 2118—2121).—The solution is just acidified with hydrochloric acid and excess of 50% acetic acid, or ammonium acetate, is added. A solution of 1 g. of 1-nitroso-β-naphthol in 50 c.c. of 50% acetic acid is then added. After some hours the precipitate of ferric 1-nitroso-β-naphthoxide is washed and ignited to ferric oxide, which is spectroscopically free from gallium. The filtrate is evaporated to dryness, the residue dissolved in hot aqua regia, boiled with hydrochloric acid, and the gallium precipitated as hydroxide, which is then ignited to oxide. The latter contains only negligible traces of iron.

S. K. Tweedy.

Rapid determination of manganese. G. Spacu and J. Dick (Z. anal. Chem., 1928, 74, 188—191).—The cold, neutral solution is treated with 1·5 g. of solid ammonium thiocyanate and 4 c.c. of pyridine. After vigorous stirring the crystalline precipitate, $Mn(SCN)_2,4C_5H_5N$, is collected in a porous filtering crucible, washed in succession with water, dilute alcohol, absolute alcohol, and ether containing small quantities of the precipitants, dried in a vacuum desiccator, and weighed; it contains 11·27% Mn. A. R. Powell.

Determination of manganese dioxide etc. by Bunsen's method. E. Rupp (Chem.-Ztg., 1928, 52, 429—430).—Manganese dioxide and fuming hydrochloric acid are heated in a 30-c.c. distillation flask, the neck of which is closed by a stopper provided with a boiling capillary; the gases evolved are passed into a solution of potassium iodide contained in a bottle closed by an absorption tube containing glass wool and potassium iodide crystals. In order to prevent "sucking back," the side tube of the flask is cut to a length of 5 cm. and 18—20 cm. of capillary tube of diameter 2·5—2·8 mm. are joined on at a suitable angle. Satisfactory results may also be obtained by distilling into alkaline arsenite or alkaline iodide solution contained in an open vessel and titrating with potassium bromate or thiosulphate after acidifying, as the case may be, provided that sodium hydroxide and not carbonate is used as the alkaline reagent. F. R. Ennos.

Volumetric analysis of chromates. P. Sokolov and T. Aristova (J. Chem. Ind. [Russia], 1927, 4, 905—906; Chem. Zentr., 1928, i, 1307).—The determination of chromate by addition of excess of ferrous sulphate and titration with permanganate is more accurate than titration of dichromate solution into ferrous sulphate, using ferricyanide as external indicator. A. A. Eldridge.

Electrometric determination of chromic acid in presence of vanadic acid by application of induction and catalysis. R. Lang and J. Swerina (Z. Elektrochem., 1928, 34, 364—367).—Chromic acid may be determined by titrating in approximately *N*-hydrochloric acid solution with arsenious oxide solution in presence of manganese sulphate; immediately before the end-point is reached 1 drop of 0·0025*M*-potassium iodide or iodate is added and the titration completed. When a mixture of chromium and vanadium is to be dealt with, the metals, including the iron which is usually present, are oxidised in acid solution to their highest valency state by hydrogen peroxide or nitric acid; a little potassium permanganate is added to the neutralised solution, which is heated to boiling, and silver nitrate, sulphuric acid, and hydrochloric acid are added. Complete reduction of the manganese takes place in a few minutes, and the solution is boiled to drive off chlorine and to coagulate the silver chloride formed. Chromium may then be determined as above, whilst the vanadium determination is carried out by the ferrous sulphate method. H. F. Gillbe.

Detection of tin, zinc, chlorine and, [bromine]. E. Eegriwe (Z. anal. Chem., 1928, 74, 225—231).—The hydrochloric acid solution of antimony and tin sulphides is evaporated to small volume. A few c.c. of concentrated hydrochloric acid are added and the whole is treated with iron to remove antimony and to reduce tin to the stannous state. A few drops of the solution are allowed to run down the sides of a test-tube containing 5 c.c. of a 0·01% solution of diazine-green S(K) previously acidified (to obtain a blue coloration) with a few drops of hydrochloric acid. After a short time a violet, and later a red, coloration appears at the surface of separation. Quantities of tin of the order of 0·002 mg. may be thus detected.

Minute quantities of zinc may be detected by the use of metanil-yellow or orange IV. To each drop of a 0·01% solution of dye are added 3 drops of a 2% solution of potassium ferricyanide. The whole is made faintly acid with mineral acid, when a red colour develops. On addition of a drop of a faintly acid solution of a zinc salt the colour disappears. If chromate is present this must first be reduced to chromium salt by treatment of the acidified solution with hydrogen peroxide. Zinc may also be detected by the use of diethylaniline. Ten drops of a solution of 0·5 c.c. of diethylaniline in 200 c.c. of 50% phosphoric acid are added to 15 drops of the ferricyanide solution. On addition of a drop of a faintly acid solution of a zinc salt the initial yellow colour gradually becomes reddish-brown. Alternatively, the diethylaniline (0·25 c.c.) may be dissolved in 200 c.c. of 1 : 1 sulphuric acid. In this case 15 drops are added to 15 drops of ferricyanide solution, to give an orange liquid yielding an orange or reddish-brown turbidity on addition of a drop of the solution of zinc salt. If the amount of zinc exceeds 0·01 mg. precipitation occurs. As before, chromate interferes and must be reduced. Cations forming coloured precipitates with ferricyanide must be excluded. Quantities of zinc of the order 0·002 mg. may be readily detected in presence of chromium and aluminium.

Quantities of chlorine of the order 0·03 mg. are detectable by the use of filter-paper treated with acid-fuchsin. The change is from red to yellow. Bromine and nitrogen peroxide interfere. Quantities of the order 0·002 mg. may be detected by the use of azo-carmine B(B) or rosindulin 2B. Papers stained red by aqueous solutions of the dyes become yellow. If the process be interrupted when still incomplete and the dried paper held for an instant in the neck of a bottle containing concentrated hydrochloric acid the yellow colour is changed to violet or blue. Bromine gives the same reaction. This reaction may be used for the detection of hypochlorites and hypobromites. The solution to be tested is added to a solution of the dye until an orange colour is produced. The solution is then acidified. Bromides can be detected in presence of chlorides by this reaction, bromine being liberated by treatment with manganese dioxide and glacial acetic acid, lead dioxide, and 2*N*-acetic acid, or potassium dichromate and dilute sulphuric acid. J. S. Carter.

Colorimetric determination of titanium by the hydrogen peroxide method. F. G. Germuth (J. Amer. Chem. Soc., 1928, 50, 1910).—The colour fading produced by phosphate ion (Faber, A., 1907, ii, 557) may be prevented by the addition of 1 c.c. of 0·1% uranium acetate solution for each 0·1 mg. of titanium. The temperature should be between 20° and 50°. S. K. TWEEDY.

Volumetric determination of germanic acid. A. TCHAKIRIAN (Compt. rend., 1928, **187**, 229—231).—An aqueous solution is prepared by boiling, the solubility being increased by adding 2 g. of mannitol per g. of germanium dioxide. The solution may then be titrated with alkali, using phenolphthalein as indicator. In the absence of mannitol, glycerol, or dextrose only about 0·4 of the germanic acid is neutralised. The mannitol–germanic acid compound liberates iodine from a mixture of potassium iodide and potassium iodate, and hence may be determined with sodium thiosulphate. Both methods have an accuracy of about 1%. The formula $H_2[Ge_2O_5M_n]$ is suggested for the mannitol–germanic acid compound, M representing mannitol, and n being at least 2. C. W. GIBBY.

Detection of vanadium, [uranium, and titanium]. J. RÖLL (Z. anal. Chem., 1928, **74**, 342—345).—The customary method for the detection of vanadium, *i.e.*, examination of the filtrate after treatment with ammonium sulphide, is held to be unsatisfactory. It is preferable to precipitate vanadium along with iron, aluminium, and chromium as the metavanadate of these metals. Uranium and titanium will, if present, be also found in the precipitate. The washed precipitate is treated with a hot solution of sodium hydroxide, when vanadium and aluminium are removed as vanadate and aluminate, respectively. The presence of vanadium is confirmed by treating a portion of the acidified filtrate with hydrogen peroxide. The residue insoluble in sodium hydroxide is treated with a hot solution of sodium carbonate. The presence of uranium in the filtrate is confirmed by adding a few c.c. of a solution of ferrocyanide and neutralising with hydrochloric acid. Iron, chromium, and titanium are detected in the insoluble residue by specific tests. Titanium is conveniently detected by dissolving in acid and testing with hydrogen peroxide in presence of phosphoric acid. The absence of vanadium should be confirmed by testing with ammonium fluoride before making the test for titanium. J. S. CARTER.

Blowpipe test for metals. O. PRÖSCHOLD (Z. physikal. chem. Unterr., 1928, **41**, 40—44; Chem. Zentr., 1928, i, 1209).—The appearance of the pellets which fall into a paper box when the material is heated on charcoal serves to differentiate antimony, bismuth, cadmium, lead, tin, zinc, silver, and Wood's alloy. A. A. ELDRIDGE.

Determination of traces of antimony in copper. H. BLUMENTHAL.—See B., 1928, 573.

Colorimetric determinations of small quantities of antimony, and their separation from tin. S. G. CLARKE (Analyst, 1928, **53**, 373—379).—To determine amounts of antimony in tin of the order 0·001—0·05%, 5 g. of tin are dissolved in 50 c.c. of concentrated hydrochloric acid, with excess of bromine while the tin is dissolving; 10 g. of oxalic acid are then added and 350 c.c. of water, the liquid is boiled, all free bromine reduced with sodium hypophosphite, and a piece of coiled cleaned copper foil 15×12 cm. added. Boiling is continued for 1·5—2 hrs., the coil removed and washed successively in 5% hydrochloric acid and water, covered with water, about 1 g. of sodium peroxide added, warmed until the deposit is dissolved, the solution poured off, and the coil tested by immersion in 1 : 1 hydrochloric acid. The antimony is precipitated by passing a current of hydrogen sulphide for 15 sec., the precipitate coagulated, and the liquid filtered. The filter is washed with a dilute solution of an electrolyte and 5 c.c. of concentrated sulphuric acid are added to the filtrate; after addition of a few drops of nitric acid near the end stage, the solution is evaporated just to fuming. After cooling, 15 c.c. of water are added and the antimony is determined colorimetrically by addition to a solution of 10 c.c. of 1% gum arabic, 5 c.c. of 20% potassium iodide, 1 c.c. of 10% aqueous pyridine, and 1 c.c. of a dilute solution of sulphur dioxide in 60 c.c. of cold dilute (1 : 3) sulphuric acid, the comparison solution requiring 80 c.c. of sulphuric acid. As little as 0·05 mg. of antimony can be determined by this method. D. G. HEWER.

Separation of iridium and rhodium by fusion with bismuth. B. KARPOV (Ann. Inst. Platine, 1928, **6**, 98—100).—Alloys containing metals of the platinum group are analysed for rhodium by fusing the residue remaining after treatment of the silver alloy with nitric acid and aqua regia with bismuth in a carbon crucible at 1000° for about 2—3 hrs., in a reducing atmosphere. The aqua regia solution of the bismuth alloy contains the rhodium, whilst the insoluble residue consists of iridium. The use of bismuth in place of lead usually used shortens the time necessary for carrying out this analysis by at least 40%. R. TRUSZKOWSKI.

Determination of osmium. E. FRITZMANN (Ann. Inst. Platine, 1928, **6**, 116—122).—See this vol., 388. R. TRUSZKOWSKI.

Nomography. IV. O. LIESCHE (Chem. Fabr., 1928, 450—451, 463—465).—Nomograms on three linear scales effect graphical addition and subtraction, on logarithmic scales multiplication and division. The first can be used for the solution of linear equations with two independent variables as in the "indirect" analysis of a mixture of antimony tri- and penta-sulphides. An example of the use of logarithmic scales is given by the determination of the volume-% of converted ammonia in the Haber process, given the pressure, temperature, and equilibrium constant. C. IRWIN.

Drying apparatus. F. FRIEDRICHS (Chem.-Ztg., 1928, **52**, 601).—A modification of Abderhalden's drying apparatus is illustrated. The connexion to the vacuum pump is joined directly to the drying chamber instead of to the container holding the drying substance, so that the drying can be conducted in a vacuum or in an atmosphere of any suitable gas. A. R. POWELL.

Aspirator. O. RODE (Chem.-Ztg., 1928, **52**, 601).—The apparatus comprises two 5—6-litre glass bottles each provided with a rubber stopper carrying a short tube with stopcock and a long tube reaching

to the bottom. The two long tubes are connected together by means of a length of rubber tubing and, when filled with water, act as a siphon to permit the transfer of water from one bottle to the other.
A. R. POWELL.

[Laboratory] gas generator. V. T. JACKSON (Ind. Eng. Chem., 1928, **20**, 771).—The aspirator which serves as generator is so attached to the acid vessel that the opening of a stopcock allows the acid to descend into the generator and its closing with the resultant gas pressure forces it back again. The apparatus also includes a large acid reservoir and a glass-wool filter for catching spray. C. IRWIN.

Saybolt-type micro-viscosimeter. S. M. ROGERS and L. R. ADKINS (Ind. Eng. Chem., 1928, **20**, 742).—The viscosimeter has a barrel of capacity 8·5 c.c. of proportions similar to the Saybolt instrument. The viscosities of a number of oils were tested with both the usual and micro instrument and ratios varying from 4·8 to 5·1 were obtained. The cooling error on the apparatus described was very slight even at 99°. C. IRWIN.

Measurement of the viscosity of fluids. R. O. BOSWALL (J. Mun. Coll. Tech. Manchester, 1928, **13**, 10—21).—A description of a robust viscosimeter giving continuous readings of the viscosity of fluids under viscous flow. The fluid under examination passes through a special nozzle from one reservoir to another, vertically below it, through a narrow tube of uniform bore. These reservoirs are fitted with pressure gauges and the viscosity of the fluid is obtained from readings of the pressures in the reservoirs, and by making reference to experimental calibration charts on which the viscosity is expressed as a function of the ratio of the pressures in the reservoirs and of the density of the fluid. F. G. TRYHORN.

Laboratory uses of monel metal. L. F. BATES and R. C. BROWN (Nature, 1928, **122**, 240).—Various uses are described. A. A. ELDRIDGE.

Carbon resistor furnaces for laboratory use. H. C. KREMERS and L. F. YNTEMA (Ind. Eng. Chem., 1928, **20**, 770—771).—A granular carbon resistor furnace constructed of concentric alundum tubes and graphite electrodes is suitable for temperatures up to 1200°, and especially for alloy research. It is best used with a step-down transformer with variable secondary winding. C. IRWIN.

Heraeus electric micro-combustion furnace. B. FLASCHENTRÄGER (Z. angew. Chem., 1928, **41**, 840—841).—The apparatus comprises three small heating units mounted in alinement on a stand in such a way that the middle and right-hand furnaces are movable along the combustion tube. The right-hand unit is fixed to the stand and is filled with cymene as a heating liquid which is maintained at 180° by an electric heating element. The combustion boat is placed in the tube about 2 cm. to the right of the middle furnace (19 cm. long), the right-hand small furnace (7 cm. long) is heated to redness and slowly moved towards the middle until combustion ceases, and, finally, this is moved back and the middle furnace moved along to cover the boat so as to ensure complete combustion. A. R. POWELL.

Valve for use with currents of gas. E. BLECHSCHMIDT (Physikal. Z., 1928, **29**, 441).—A new type of glass valve is described simplifying the regulation of a stream of gas. It is constructed in the form of a tap, the lower portion of the barrel forming one lead and a side tube the other. The key is not bored, but is ground in such a manner that the upper part forms a seal against the atmosphere, whereas the lower portion separates the two sides of the apparatus only when in one position, other positions enabling gas to stream through from one part of the apparatus to another at a known rate. A scale attached to the barrel enables comparative experiments to be carried out. J. W. SMITH.

Adjustable needle valve leaks. C. T. KNIPP (Nature, 1928, **122**, 131).—Three forms of needle valve, one of which admits of calibration, and all being constructed with very long and narrow needles, are described and figured. A. A. ELDRIDGE.

Electric crucible furnace with air-inlet at the bottom. G. ABELS and E. TITOV (Ann. Inst. Polyt. Ural, 1927, **6**, 351—352).—The laboratory furnace described consists of a threaded cylinder 5 cm. in diameter on which a chromium–nickel wire is wound. The inner space is connected with the air by channels in the double cover and in the foot. By displacement of a disc the air supply may be regulated or completely stopped. A current of 3 amp. at 120 volts gives the temperature 950°. The furnace is patented.
T. H. POPE.

Physical methods in the chemical laboratory. V. Production and measurement of high temperatures. E. SCHRÖER (Z. angew. Chem., 1928, **41**, 757—760).—A review of the different methods of producing and measuring high temperatures. Heating by the burning of gaseous mixtures (*e.g.* oxygen–hydrogen flame), the recombination of atomic hydrogen, the explosion of gaseous mixtures, the "thermite" process, resistance ovens, induction furnaces, the concentration of cathode rays on a substance to be heated, and the use of the electric arc are described. For measurement, the use of the gas thermometer, resistance thermometer, thermo-couple, and optical pyrometer are described, and a special method depending on the thermionic emission from a filament is mentioned. A. J. MEE.

Laboratory condenser. E. S. WEST (Ind. Eng. Chem., 1928, **20**, 737).—A condenser is constructed of an inner tube of light Pyrex glass sealed at each end to a jacket of thicker glass carrying an adapter. The narrow space between the two tubes renders cooling very efficient. C. IRWIN.

Pressure regulation in vacuum distillation. G. H. RICHTER (Ind. Eng. Chem., 1928, **20**, 682).—As the b. p. of a substance is usually recorded only under one pressure some convenient means of adjusting the pressure to this point in a distillation under reduced pressure is desirable. This is given by the needle valve of a Tirrill burner well greased and connected to the vacuum line by thick suction tubing and a T-piece. C. IRWIN.

Apparatus for sampling powdered solids. J. VON MEERSCHEIDT-HÜLLESSEM.—See B., 1928, 589.

Automatic sample-collecting vacuum pump. E. R. Weaver and M. Shepherd (J. Amer. Chem. Soc., 1928, **50**, 1829—1835).—An automatic Töpler pump is arranged as the backing unit of a high-speed mercury-vapour pump; the mercury delivered by the former is restored to the cycle by the alternate application of vacuum and atmospheric pressure to the pump reservoir by means of an auxiliary system operating on the suction of a water aspirator or a mechanical vacuum pump. The gas pumped out is automatically collected. Stopcocks are eliminated from the pumping cycle. S. K. Tweedy.

Device for the preparation of solutions of constant density. J. Hamous.—See B., 1928, 589.

Rapid evaporation at the ordinary temperature. E. Jantzen and H. Schmalfuss.—See B., 1928, 589.

Calorimeter for determination of heats of combustion. A. Eucken and L. Meyer.—See B., 1928, 589.

Method for detecting leaks in glass vacuum apparatus. P. Selenyi (Z. Physik, 1928, **48**, 733—734).—The residual gas inside the vacuum apparatus is excited by a Tesla current while another gas leaks into the apparatus. If the light emitted by the two gases is markedly different, as with carbon dioxide and air, the leaking spot can be detected directly by the change in colour in its vicinity. J. W. Smith.

Action of the Geiger counter. L. F. Curtiss (Physical Rev., 1928, [ii], **31**, 1060—1071).—When the point of the Geiger point counter is negative, the sensitive surface is on the point. A sensitive surface is obtained only when the point has been treated with a catalyst, *e.g.*, iron oxide, copper oxide, or platinum or palladium-black, which may be poisoned by mercury, sulphur dioxide, or hydrogen sulphide. The adsorbed gas layer plays an important part in the action of the counter. A. A. Eldridge.

Apparatus for determining mol. wt. by the b.-p. method. H. Rupe and N. Vassliev (Helv. Chim. Acta, 1928, **11**, 713—716).—The apparatus described is easy to construct and is suitable for ordinary laboratory use. The method can be used for a variety of solutes in such solvents as water, acetone, benzene, and chloroform with an error not greater than 10% and usually much less; the longest time required for a determination is 1 hr. L. S. Theobald.

Determination of mol. wts. by the Barger–Rast method. A. Friedrich (Mikrochem., 1928, **6**, 97—102).—The original method of Barger (J.C.S., 1904, **86**, 286) is shown to give more satisfactory results than the modification proposed by Rast (A., 1921, ii, 623). An alternative procedure is to use a tube drawn out to a capillary at both ends; this is half filled with the standard solution by suction, a small air bubble is admitted, and the remainder of the tube is filled with the test solution by continuing the suction. Both capillary ends are then sealed and the observation of the movement of the bubble is carried out as usual. Various precautions for obtaining accurate results are described and sources of error in the three modifications are discussed. A. R. Powell.

Magnetic micro-balance. E. Wedekind (Z. angew. Chem., 1928, **41**, 771—774).—The construction of an instrument for magneto-chemical work, in which the ordinary analytical balance previously used is replaced by a micro-balance, is described. The electro-magnets are also greatly improved. The method of using the balance is described. The reproducibility of the instrument for differences in weight in the same field is in general ±0·002 mg. For powders the susceptibility can be estimated to within about 1%. A. J. Mee.

Apparatus for micro-filtration. K. L. Maljarov (Mikrochem., 1928, **6**, 103—105).—The apparatus comprises two pieces of thick-walled glass tubing, the lower end of the longer piece and the upper end of the shorter piece being thickened and ground flat so as to form a perfect joint between the two. The lower end of the shorter piece is drawn out to a capillary jet and the two pieces are held together with a bow-shaped spring clamp after inserting a small piece of any type of filter-paper between them. The filter is placed with the jet in the liquid and suction is applied by means of the mouth at the upper end. The filtrate collects above the paper and the collecting tube may, if desired, be provided with a small bulb to increase its capacity. A. R. Powell.

Ultrafiltration. R. Wasmuht (Chem. Fabr., 1928, 405—406).—Amongst the advantages of the membrane filter is that adsorption effects, such as the staining brown of filter paper by iron bromide solution from the formation of basic salt, do not occur. Two methods of securing a membrane filter held between two filter papers and resting on a perforated porcelain plate are described. Another apparatus is designed for the treatment of steel turnings with bromine solution and the ultrafiltration of the insoluble residue, with exclusion of air. C. Irwin.

Self-acting filters. J. V. Dubský and A. Rabas (Chem. Weekblad, 1928, **25**, 293—294).—Forms of apparatus are described, based on the method in which the material to be filtered is contained in a closed vessel inverted with its mouth below the level of the liquid in the filter funnel, in which the necessity of removing the closed vessel for refilling is obviated. S. I. Levy.

Automatic addition of a fluid. W. P. Jorissen (Chem. Weekblad, 1928, **25**, 294—295; cf. preceding abstract).—Several very early forms of apparatus, designed to secure the continuous flow of liquid to a filter, are recalled; the original form is attributed to Berzelius. S. I. Levy.

Burette for titration. N. M. Ketov (Ann. Inst. Polyt. Ural, 1927, **6**, 355—356).—A stopcock in the upper end of a constricted (jet) tube is connected by means of a rubber tube with the exit tube of a stoppered flask into which passes the jet of a burette. The volume of liquid run (without contact with rubber tube or stopcock grease) from the constricted tube is equal to that of the distilled water which is thereby drawn from the burette into the flask. The pinchcock may be placed between the burette and the flask. The constricted tube is filled from the top after removal of the ground-in cap and stopcock, and closure of the jet with rubber tubing and a glass plug.
T. H. Pope.

Weight burette for the micro-measurement of liquid volumes. M. Shepherd (U.S. Bur. Stand., Sci. Papers, No. 555, 1927, **22**, 287—292).—Volume is measured by determining the weight of mercury used to displace the liquid concerned. Liquids are condensed into the evacuated burette by subjecting a portion of the burette to liquid-air temperatures. The method is applicable to liquids the vapour pressures of which are not excessive at the ordinary temperature. It is accurate to within 0·001 c.c. J. S. Carter.

Hartmann and Braun's spring balance. J. E. Verschaffelt and E. van de Casteele (Natuurwetensch. Tijds., 1928, **10**, 35—46).—The balance is described, and the relation between load and reading under ordinary working conditions considered mathematically. The influence of temperature is important, and varies linearly with the load. A method of calibrating is described, and the effect of altering the adjustments examined. S. I. Levy.

High-resistance liquid. A. Gyemant (Z. tech. Physik, 1927, **8**, 491—493; Chem. Zentr., 1928, i, 734).—A solution of a strong electrolyte in a mixture of two organic solvents of differing dielectric constant, *e.g.*, picric acid in benzene and alcohol, gives a liquid the high resistance of which (10^4—10^{12} ohms) can be varied within wide limits. Applications are described. A. A. Eldridge.

Continuous extractor. D. Henville (Analyst, 1928, **53**, 380—382).—An apparatus suitable for the extraction of about 50 g. of material consists of a wide glass extractor (*a*), tapering at the bottom to a narrow tube, bent round and inserted into a rather wider tube which connects from a higher point in (*a*) to the extraction flask below. The apparatus is attached to a reflux condenser, and is packed at the bottom of (*a*) with cotton wool or asbestos, or a thimble may be used. Space is left for formation of a " head " and the material being extracted is always totally immersed in solvent, but the quantity of the latter must not be sufficient to overflow through the large side tube. D. G. Hewer.

Method of heating extraction apparatus. S. Reiner (Chem.-Ztg., 1928, **52**, 529).—Six separately controlled electric hot plates arranged on a rack serve the same number of Soxhlet extractors. These are held by hinged clamps allowing the condensers to be lifted and the flasks removed. C. Irwin.

Constant-drop apparatus. A. H. Burr (J. Soc. Dyers and Col., 1928, **44**, 18—19).—The apparatus consists of an inverted bell-jar, or a wide-mouthed bottle with the bottom cut away, fitted with a rubber stopper carrying two tubes. The first tube, the outflow to waste, controls the height of water in the vessel. The second tube, which rises sufficiently above the bottom of the reservoir to avoid dirt carried in by the water supply, is connected by rubber tubing to a capillary tube previously tested to give approximately the desired number of drops per min. Agitation of the water in the reservoir is prevented as far as possible by carrying the water inlet tube practically to the bottom, and reducing the inflow to the minimum to maintain the constant level. Constancy of dropping is maintained indefinitely if the head of water is maintained constant and the water supply kept free from dirt. R. Brightman.

Preparation and use of the hydrogen electrode. S. Popoff, A. H. Kunz, and R. D. Snow (J. Physical Chem., 1928, **32**, 1056—1060).—Various conditions affecting the preparation of hydrogen electrodes have been studied. The electrode should be cleaned by electrolysing as anode in concentrated hydrochloric acid to remove the old deposit, and then plated with gold by electrolysis in Clark's cyanide solution. This plating does not affect the time of attainment of equilibrium but results in a more adherent coating of platinum, which is also more easily removed on cleaning. The electrode is then used as cathode for 5 min. in 3% chloroplatinic acid containing 0·5 c.c. of 0·1*N*-lead acetate in 100 c.c., with a current density of 1·35 amp. per dm.^{2}, electrolysed in dilute sodium hydroxide for a few seconds and then in dilute sulphuric acid for 1 min. The lead acetate is essential for a good deposit. The electrode attains equilibrium more quickly in a Bovie titration cell than in an open beaker. Thinly-coated electrodes are preferable to those thickly coated, since the latter require greater time for the attainment of equilibrium and are more susceptible to poisoning. Treatment with nitric acid or dichromate cleaning mixture removes poisoning due to mercuric chloride, but with the repurified chemicals used, poisoning of the electrodes was difficult to effect. The maximum variation in potential of electrodes prepared by the above method was $\pm$0·1 millivolt. L. S. Theobald.

Oxygen electrode as a quasi-quantitative instrument. W. T. Richards (J. Physical Chem., 1928, **32**, 990—1005).—The preparation of an oxygen–platinum electrode giving reproducible results is discussed, and a cell chain having a flowing junction and requiring small volumes of liquid is described. The electrode surface should be as large as possible with a constant area immersed, and solutions not easily reduced, such as phosphate or borate, should be employed if reproducible results are to be obtained. Nitrate and sulphate solutions show a continuous fall in potential. Under suitable conditions, oxygen electrode potentials constant to 1 millivolt for many days, but below the thermodynamic value for the oxygen–hydrogen, can be obtained. The oxygen potential varies quantitatively with the partial pressure of gaseous oxygen between 0 and 1 atm. Details are given of a method for measuring activities of the hydroxyl ion with an accuracy of a few millivolts. The effect of increasing concentration of electrolytes on the potential of the hydrogen–oxygen chain has also been measured. L. S. Theobald.

Determination of the m. p. of paraffins and the preparation of paraffin mixtures of definite m. p. J. Kisser (Z. wiss. Mikros., 1927, **44**, 443—451; Chem. Zentr., 1928, i, 1204—1205).—Halle's method for the determination of m. p. of paraffins is very accurate, although the ordinary capillary method is good. Formulæ are given for the preparation of mixtures of definite m. p. A. A. Eldridge.

Demonstration of crystallisation processes by the streak method. I. II. W. Kraemer (Z. wiss. Mikros., 1927, **44**, 476—477, 477; Chem. Zentr., 1928, i, 1206).

Geochemistry.

Inter-relation between diatoms, their chemical environment, and upwelling water in the sea, off the coast of Southern California. E. G. Moberg (Proc. Nat. Acad. Sci., 1928, **14**, 511—518).

Dissolved and suspended mineral matter in Colorado River. W. D. Collins and C. S. Howard (Ind. Eng. Chem., 1928, **20**, 746—748).—In 1925—1927 the dissolved solids varied from 250 to 1500 in 10^6, the total hardness calculated as calcium carbonate ranged from 130 to 640 in 10^6, and the non-carbonate hardness from 38 to 400 in 10^6.

R. A. Pratt.

Rare gases from thermal springs and the earthquakes of April 14 and 18, 1928, in Bulgaria. N. P. Péntchev (Compt. rend., 1928, **187**, 243—244).—The composition of rare gases evolved from thermal springs in Bulgaria has been found to be unchanged by earthquakes. No certain conclusion can be reached concerning the constancy or otherwise of their radioactive properties. C. W. Gibby.

Probable identity of gageite with tephroite. S. G. Gordon (Proc. Acad. Nat. Sci. Philadelphia, 1928, **79** (for 1927), 207—208).—A tabulation of the chemical composition, optical data, crystal angles, etc. of gageite from Franklin Furnace, New Jersey (A., 1910, ii, 968), suggests that this mineral is the same as tephroite. L. J. Spencer.

Arfvedsonite, riebeckite, and crocidolite from Greenland. S. G. Gordon (Proc. Acad. Nat. Sci. Philadelphia, 1928, **79** (for 1927), 193—205).—Descriptions with optical data are given for these amphiboles from the nepheline-syenites of south Greenland. The following analyses are given of arfvedsonite from different localities. I by H. S. Washington, II by E. V. Shannon, and III by F. Wynkoop. They are interpreted as mixtures of the arfvedsonite molecule ($R_2O,3RO,4SiO_2$) and riebeckite molecule ($R_2O,R_2O_3,4SiO_2$), usually with an excess of R_2O_3, where R_2O is largely Na_2O, and RO and R_2O_3 are chiefly FeO and Fe_2O_3.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.
I.	43·52	1·73	5·30	11·12	22·39	1·13	1·09
II.	43·08	0·83	4·44	8·06	28·97	0·70	0·32
III.	49·11	0·78	1·16	9·23	25·50	1·13	0·18

	CaO.	Na_2O.	K_2O.	F.	H_2O.	Total.	*d*.
I.	2·21	7·39	1·83	0·88	1·20	100·26	3·465
II.	4·08	5·88	3·28	—	1·10	100·74	3·447
III.	0·77	8·01	2·89	0·29	1·12	100·05	4·410

Totals less O for F_2. I, also ZrO_2 0·84. II, also BaO trace.

Riebeckite occurs in parallel growth on ægirine crystals, and crocidolite in parallel growth on arfvedsonite. L. J. Spencer.

Olivine of Linosa (Pelagic Islands). G. Carobbi (Atti R. Accad. Lincei, 1928, [vi], **7**, 654—660).—Crystallographic and analytical data are given for two specimens of transparent olivine, one greenish-yellow (*d* 3·410), the other reddish-yellow (*d* 3·462). These contained respectively: FeO, 12·43 and 11·06%; NiO, 0·12 and 0·18%; CoO, 0·13 and 0·10%; and, more noteworthy, PbO, 0·20 and 0·26%. It is suggested that the lead occurs as the result of an isomorphic substitution of magnesium. The two compounds $(Fe,Co,Ni,Mn)_2SiO_4$ and $(Mg,Ca,Pb)_2SiO_4$ constitute 77·5% and 22·5%, respectively, of the specimens analysed. F. G. Tryhorn.

Intrusive rock of Muno (Luxemburg) and metamorphism produced by it. A. L. Hacquaert (Natuurwetensch. Tijds., 1928, **10**, 73—88).—The intrusive veins consist chiefly of felspar and biotite, with inclusions of calcite, quartz, apatite, zircon, chlorite, and pyrites, and the material is classed as a kersantite. The inclusions of calcite are of magmatic origin. It is deduced that the intrusions occurred at relatively low temperatures, and that the whole was subsequently subjected to hydrothermal action. The action of the solutions, which were rich in magnesium salts, has resulted in considerable impregnation of the surrounding rock with biotite.

S. I. Levy.

Series of lavas of Southern Serbia. J. Tomitch (Compt. rend., 1928, **187**, 133—136).—Analyses of five specimens are recorded. C. W. Gibby.

Alkali-lavas from Mount Nimrud, Armenia. G. T. Prior (Min. Mag., 1928, **21**, 485—488).—Micro-sections of rocks from Mount Nimrud showed the presence of anorthoclase, ægirine, and soda-amphiboles. Complete chemical analyses were therefore made of three of the rocks (soda-rhyolite, pantelleritic trachyte, and trachyandesite), showing about 6% Na_2O, and a relation to the soda-rocks of the Rift Valley in East Africa is suggested.

L. J. Spencer.

Julienite. A. Schoep (Natuurwetensch. Tijds., **10**, 58—59).—Blue microscopic needles, forming a thin layer on a white talcose schist at Chamibumba, near Katanga, having refractive indices of 1·645 parallel to and 1·556 perpendicular to the elongation, respectively, and readily soluble in cold water, appear to consist of a hydrated cobalt chloronitrate.

S. I. Levy.

Organic Chemistry.

Steric hindrance. W. Hückel (Ber., 1928, **61**, [*B*], 1517—1524).—An attempt is made to differentiate between the spatial and chemical factors generally confusedly involved under the term "steric hindrance." The modified Trautz formula $k=\alpha e^{-q/RT}$ is used in which *q*, the activation energy (mean energy required to bring the reacting molecule into the active condition), is usually calculated from the temperature coefficient of the velocity coefficient *k*. The "action constant" α, which expresses the probability of encounter of the active surfaces of the molecules and, in addition to the activation energy, controls the velocity coefficient, is obtained by substituting the calculated value of *q* in the value of *k* determined at any definite temperature. Examination of the data recorded by Vavon for the hydrolysis of the *cis*- and *trans-o-iso*propyl*cyclo*hexyl hydrogen succinates, *cis*- and *trans-o-n*-propyl*cyclo*hexyl hydrogen phthalates, and bornyl and *iso*bornyl hydrogen phthalates shows that considerable differences in the rates of reaction may depend on great differences between *q* or α but a uniform interpretation of steric hindrance cannot be deduced from the results. Examination of the rates of hydrolysis of *n*-propyl, *n*- and *iso*-butyl, *iso*amyl, *iso*propyl, *sec.*- and *tert.*-butyl acetates shows that the activation energy and action constants are approximately the same for esters of primary alcohols. The activation energy of esters of tertiary alcohols is much greater and the action constants are much smaller than those of esters of primary alcohols, both influences diminishing the rate of hydrolysis. H. Wren.

Thermal dissociation of ethane, propane, *n*- and *iso*-butane. R. N. Pease (J. Amer. Chem. Soc., 1928, **50**, 1779—1785).—The gases are passed through Pyrex glass tubes at 625° and 650° under 1 atm. pressure. The total rate of dissociation increases with the complexity of the molecule. The two main reactions are dehydrogenation and demethanation. The ratios of hydrogen to methane decrease in the sequence, ethane, propane, *n*-butane. *iso*Butane decomposes at about the same rate as *n*-butane but gives relatively much more hydrogen. *n*-Butane does not undergo appreciable secondary reaction. Reactions appear to be somewhat more rapid than normal in the first few seconds, but dilution experiments indicate a change of the first order. The temperature coefficients are, as a minimum, 1·5—2 per 25°, giving a minimum activation energy of 25,000—50,000 g.-cal. H. Wren.

Control of the mol. wt. of liquid hydrocarbons produced by electrical discharge in ethane. S. C. Lind and G. Glockler (J. Amer. Chem. Soc., 1928, **50**, 1767—1772).—Silent, corona, and high-frequency discharges all cause the condensation of ethane to liquid products with liberation of permanent gases. The average mol. wt. of the liquid products has been regulated between 467 and 105 by controlling the time that the first products, either gaseous or liquid, are allowed to remain in the discharge tube. Prolongation of the action causes increase in mol. wt. of the products. H. Wren.

Wurtz reaction. Factors involved in the preparation of octane. H. F. Lewis, R. Hendricks, and G. R. Yohe (J. Amer. Chem. Soc., 1928, **50**, 1993—1998).—A method has been developed for preparing octane, b. p. 124·2—124·8°, d_4^{20} 0·7044, n_D^{20} 1·3961, from *n*-butyl bromide and sodium in 65—70% yield based on the butyl bromide. Optimal conditions consist in the use of an excess of sodium which need not exceed 50%, a volume of ether two and a half times that of the butyl bromide, low temperature, a period appropriate to each set of conditions, and fine sodium wire. Agitation is of material advantage. Traces of water are unexpectedly detrimental, but sufficient dehydration is secured if the ether is dried over calcium chloride and distilled over sodium. The presence of acetonitrile does not favour the formation of octane. Butene and at least two higher saturated hydrocarbons, possibly dodecane and hexadecane, are also produced. H. Wren.

Hexa-*tert.*-butylethinylethane. P. L. Salzberg and C. S. Marvel (J. Amer. Chem. Soc., 1928, **50**, 1737—1744).—The hydrocarbon is undissociated at the ordinary temperature and undergoes rearrangement when the temperature is raised. Cleavage by alkali metals indicates that the stability of the central ethane linking is intermediate between that of the corresponding linking in dibenzyl and hexaphenylethane.

tert.-Butylacetylene is converted by the successive action of magnesium ethyl bromide and ethyl chloroformate into *tri*-tert.-*butylethinylcarbinol*, $(CMe_3\cdot C{\vdots}C)_3C\cdot OH$, m. p. 100—102·2° (corr.) (additive *compound* with stannic chloride), which is isomerised by concentrated sulphuric acid to the *ketone* $(CMe_3\cdot C{\vdots}C)_2\cdot C{:}CH\cdot CO\cdot CMe_3$, m. p. 109·5—110·5° (corr.). The carbinol in light petroleum is transformed by phosphorus tribromide into the corresponding *bromide*, apparently existing in two forms, m. p. 69—70° (corr.) and 177—178° (corr.), respectively. *Tri*-tert.-*butylethinylmethyl acetate*, m. p. 144·5—145·5° (corr.), from the carbinol, potassium, and acetic anhydride or from the bromide and silver acetate, is hydrolysed by potassium ethoxide to the original carbinol. With molecular silver in the presence of ether the bromide affords *hexa*-tert.-*butylethinylethane*, $(CMe_3\cdot C{\vdots}C)_3C\cdot C(C{\vdots}C\cdot CMe_3)_3$, m. p. 130—131° (corr.), rearranged in xylene at 140° to a *hydrocarbon*, $C_{38}H_{54}$, m. p. 174—175° (corr.). *Tri*-tert.-*butylethinylacetic acid*, $(CMe_3\cdot C{\vdots}C)_3C\cdot CO_2H$, m. p. 202—205°, is prepared from the ethane by the successive action of sodium–potassium alloy and carbon dioxide or from the bromide by treatment with magnesium and carbon dioxide. H. Wren.

Action of nascent thiocyanogen on isoprene and dimethylbutadiene. H. A. Bruson and W. A. Calvert (J. Amer. Chem. Soc., 1928, **50**, 1735—1737).—An additive *compound*, $C_7H_8N_2S_2$, m. p. 76—77° (corr.), is formed by the addition of bromine to isoprene and sodium thiocyanate in glacial acetic acid at 5—6°. A similar *substance*, $C_8H_{10}N_2S_2$, m. p. 130° (corr.), is produced from $\beta\gamma$-dimethylbutadiene. The compounds are useful for the identification of the hydrocarbons. H. Wren.

Rearrangements of the triple linking. H. H. Guest (J. Amer. Chem. Soc., 1928, **50**, 1744—1746).—Δ^{α}-Heptinene is prepared in 74% yield by the addition of dibromoheptane to finely-divided potassium hydroxide covered with mineral oil at 250°. It is converted into an isomeric hydrocarbon by passage over soda–lime at 380° or over pumice at 350°. The reverse transformation is apparently effected by sodamide suspended in mineral oil at 160°. H. Wren.

Modification of the Adams' method of preparing alkyl iodides. H. S. King (Proc. Nova Scotian Inst. Sci., 1927, **16**, 87—91).—A modified form of apparatus is described which can be constructed from commonly available parts. H. Wren.

Colorimetric determination of ethylene chlorohydrin. M. B. Sapadinski (Z. anal. Chem., 1928, 74, 273—275, and J. Russ. Phys. Chem. Soc., 1928, 60, 695—697).—The solution containing ethylene chlorohydrin is mixed with diazobenzenesulphonic acid and warmed to 25°, whereby complete oxidation of the $\cdot CH_2\cdot OH$ group to $>C\!:\!O$ occurs. The alkali hydroxide, which induces condensation, is not added until the first change is complete; subsequently the mixture is heated at 50°. For measurement, a solution of " Bordeaux-Lafitte " in benzene, standardised by use of known amounts of ethylene chlorohydrin, is employed. H. Wren.

Derivatives of *n*-heptane. R. T. Dillon and H. J. Lucas (J. Amer. Chem. Soc., 1928, **50**, 1171—1714).—*Heptan-δ-ol*, m. p. −37·2° to −41·5°, b. p. 153·4—154·4° (corr.)/745 mm., d_4^{25} 0·8175, n_D^{25} 1·4173, is prepared from magnesium *n*-propyl bromide and ethyl formate. *Heptan-γ-ol*, from magnesium *n*-butyl bromide and propaldehyde, has b. p. 152·7—154° (corr.)/745 mm., n_D^{20} 1·4201. H. Wren.

Constitution of phytol. F. G. Fischer [with K. Löwenberg] (Annalen, 1928, **464**, 69—90).—The ketone obtained by Willstätter and co-workers (A., 1911, i, 144; 1919, i, 448) by the oxidation of phytol, and regarded by them as having the formula $C_{17}H_{34}O$, is now shown to be $C_{18}H_{36}O$, since glycollaldehyde is formed when phytol ozonide, a C_{20} compound, is reduced either by means of zinc and acetic acid or by means of hydrogen and palladised calcium carbonate. If phytol is regarded as being built up of reduced isoprene units, it is most likely to be (cf. geraniol and farnesol) γηλο-tetramethyl-Δ^{β}-hexadecen-α-ol, $CHMe_2\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_3\cdot CMe\!:\!CH\cdot CH_2\cdot OH$, which when ozonised etc. would produce glycollaldehyde and ζκξ-trimethylpentadecan-β-one. The latter substance has accordingly been synthesised: Hydrogenation of farnesol in methyl alcohol in presence of palladised calcium carbonate affords a 40%, whilst hydrogenation in 80% methyl alcohol in presence of palladous chloride gives not less than an 80% yield of *farnesane* [*βζκ-trimethyldodecane*], b. p. 119·5—120°/11 mm., d_4^{25} 0·7682, n_4^{25} 1·4303. Reduction of farnesyl acetate in ethyl acetate in presence of palladised calcium carbonate gives a little farnesane, but mainly the desired *hexahydrofarnesol* [*γηλ-trimethyldodecanol*], b. p. 151—152·5°/10 mm., d_4^{25} 0·8491, n_D^{25} 1·4487. The latter is converted by phosphorus tribromide in light petroleum into *γηλ-trimethyldodecyl bromide*, b. p. 150—154°/10 mm., which with ethyl sodioacetoacetate gives *ethyl γηλ-trimethyldodecylacetoacetate*, b. p. 192—195°/10 mm. The latter, when hydrolysed by cold and then by warm 3% methyl-alcoholic potassium hydroxide, affords ζκξ-trimethylpentadecan-β-one, identical in properties with the ketone, $C_{18}H_{36}O$ (b. p. 173·5—174°/10 mm. or 294—295°/708 mm., d_4^{25} 0·8323, n_D^{25} 1·4432). The two semicarbazones melted alone, or when mixed, at 66—67°. The ketone and phytol therefore have the constitutions mentioned above. E. E. Turner.

Spatial configuration of two *cis–trans*-ethylenic isomerides [βε-dimethyl-Δ^{γ}-hexene-βε-diols]. Bourguel and Rambaud (Compt. rend., 1928, **187**, 383—384).—The *trans*(α)-form, m. p. 76—77°, of βε-dimethyl-Δ^{γ}-hexene-βε-diol (Zalkind, A., 1923, i, 176) is shown to be a solid solution of 5 parts of the *cis*(β)-form, m. p. 69—70°, and 1 part of the true trans(γ)-*modification*, m. p. 101°, obtained also by reducing βε-dimethyl-Δ^{γ}-hexinene-βε-diol with sodium and alcohol. Whilst dehydration of the *cis*-modification gives a γ-oxide (Zalkind, *loc. cit.*), the *trans*-compound affords a mixture of βε-dimethyl-$\Delta^{\gamma\epsilon}$-hexadien-β-ol and βε-dimethyl-$\Delta^{\alpha\gamma\epsilon}$-hexatriene. H. Burton.

Condensations of glycerol. Rangier (Compt. rend., 1928, **187**, 345—346).—The action of fused sodium acetate on heated 95% glycerol followed by treatment of the product with acetic anhydride affords the following compounds: *diglyceryl tetra-acetate*, $(C_3H_5)_2O(OAc)_4$, b. p. 164—165°/2 mm.; *triglyceryl penta-acetate*, $(C_3H_5)_3O_2(OAc)_5$, b. p. 194—195°/2 mm.; *tetraglyceryl hexa-acetate*, b. p. 224—225°/2 mm.; *pentaglyceryl hepta-acetate*, b. p. 254—255°/2 mm.; *hexaglyceryl octa-acetate*, b. p. 284—285°/2 mm.; *heptaglyceryl nona-acetate*. H. Wren.

Acetylenic glycerols containing a straight chain of five carbon atoms. R. Lespieau (Bull. Soc. chem., 1928, [iv], **43**, 607—662).—*δε-Dichloro-Δ^{α}-pentinen-γ-ol*, b. p. 90—91°/12 mm., d^{23} 1·306, n_D 1·500, is obtained from dimagnesium acetylenyl bromide and acraldehyde dichloride. It is converted by 10% potassium hydroxide into *ε-chloro-γδ-oxido-Δ^{α}-pentinene*, b. p. 58—60°/20 mm., d^{23} 1·159, n_D 1·472, which is hydrated to *ε-chloro-Δ^{α}-pentinene-γδ-diol*, b. p. 131—132°/16 mm., d^{16} 1·289, n_D^{16} 1·501. The latter substance with sodium methoxide affords *ε-methoxy-Δ^{α}-pentinene-γδ-diol*, b. p. 100°/3 mm., d^{17} 1·12, n_D^{17} 1·473, whereas it is hydrolysed by water in presence of calcium carbonate to *Δ^{α}-pentinene-γδε-triol*, b. p. 156—159°/4 mm., d^{25} 1·217, n_D^{25} 1·489 (*triphenylurethane*, m. p. 204—206°). All the acetylenic compounds react with alcoholic silver nitrate, whereas only the dichlorohydrin and epichlorohydrin yield precipitates with ammoniacal cuprous chloride. The isolation of two *αβηθ-tetrachloro-Δ^{δ}-octinene-γζ-diols*, m. p. 139—139·5° and 96·5—97·5°, respectively, is described.

ε-Methoxy-αβ-oxido-Δ^{γ}-pentinene, b. p. 75—76°/15 mm., d^{26} 4·024, n_D^{26} 1·4573, is prepared from chloroacetaldehyde and the compound $OMe\cdot CH_2\cdot C\!:\!C\cdot MgBr$. It is converted by hydrogen chloride into *α-chloro-ε-methoxy-Δ^{γ}-pentinene-β-ol*, b. p. 117·5—118·5°/12 mm., d^{24} 1·172, n_D^{24} 1·485, and by water into *ε-methoxy-Δ^{γ}-pentinene-αβ-diol*, b. p. 155—156°/12 mm., d^{22} 1·1274, n_D^{22} 1·481; with boiling methyl alcohol containing a little sulphuric acid it affords *αε-dimethoxy-Δ^{γ}-pentinene-β-ol*, b. p. 207—210°/10 mm., d^{23} 1·0508, n_D^{23} 1·4608. *γδ-Dibromo-ε-methoxy-Δ^{γ}-pentinene-αβ-diol* has m. p. 51—52°, b. p. 192°/11 mm. H. Wren.

Use of magnesium alkoxides in the preparation of ethers. V. Cerchez (Bull. Soc. chim., 1928, [iv], **43**, 762—768).—When treated on a brine-bath with 2 mols. of methyl sulphate, magnesium alkoxides afford methyl ethers in 70—80% yield. With ethyl sulphate at 120—130° the corresponding

ethyl ethers are obtained in 60% yield. The following ethers have been prepared by this method: methyl *n*-butyl ether, b. p. 70°; methyl *iso*amyl ether, b. p. 90—91°; methyl *cyclo*hexyl ether, b. p. 133—135°; *methyl* sec.-*octyl ether*, b. p. 158° (yield 15%), octene, b. p. 125°, being also produced; ethyl *n*-propyl ether, b. p. 63·6°; ethyl *n*-butyl ether, b. p. 91°. Magnesium benzyloxide and methyl sulphate give no definite product. The alkoxides are readily obtained by treating magnesium amalgam, prepared in the dry way, with the alcohol, the action proceeding very readily with propyl and benzyl alcohols and *cyclo*hexanol, less readily with butyl, *iso*amyl, and octyl alcohols. When *cyclo*hexanol is heated at 120° with 2 mols. of methyl alcohol and 1 mol. of sulphuric acid a considerable amount of *cyclo*hexene is formed.
R. Brightman.

Hydrogenation of ethers. A. Marty (Compt. rend., 1928, **187**, 47—49).—Propyl, *iso*propyl, butyl, amyl, and *iso*amyl ethers suffer fission when passed with hydrogen over reduced nickel at 250—300°. At 180°, phenetole is smoothly converted into *cyclo*hexane and ethyl alcohol, whereas at 250° this reaction is accompanied by the production of ethane and phenol. β-Naphthyl methyl and ethyl ethers decompose at 280° in both directions; the aromatic components are further hydrogenated to di- and tetra-hydronaphthalene and tetrahydro-β-naphthol. Guaiacol at 180° under 300 mm. gives the mixed ether $OH{\cdot}C_6H_{10}{\cdot}OMe$, together with pyrocatechol and phenol (partly reduced to *cyclo*hexanol). Under similar conditions, diphenyl ether affords di*cyclo*hexyl ether, phenol, *cyclo*hexanol, benzene, and *cyclo*hexane.
H. Wren.

Action of disilicon hexachloride on ether. S. Kipping and R. A. Thompson (J.C.S., 1928, 1989—1990).—Disilicon hexachloride, like silicon tetrachloride (Kipping and Murray, this vol., 79), reacts to a slight extent with pure ether to yield a compound from which alcohol is formed on hydrolysis with sodium hydroxide. It is suggested that an additive compound is first formed which is partly decomposed into ethyl chloride and chloroethoxysilicon derivatives. J. W. Baker.

Preparation of normal sulphuric esters. R. Levaillant (Compt. rend., 1928, **187**, 234—236).—Alkyl sulphates are prepared by the action of alkyl nitrites on alkyl chlorosulphonates, $Cl{\cdot}SO_2{\cdot}OR+O{:}N{\cdot}OR'=OR{\cdot}SO_2{\cdot}OR'+NOCl$. Thus methyl chlorosulphonate and methyl nitrite at 80—145° give methyl sulphate in 40% yield. Ethyl sulphate, in 55% yield, is derived from ethyl nitrite and ethyl chlorosulphonate at 80—100°. H. Wren.

Organic titanous compound and the preparation of solutions of titanous salts. D. W. MacCorquodale and H. Adkins (J. Amer. Chem. Soc., 1928, **50**, 1938—1939).—Tetraethyl titanate is reduced by sodium and ethyl alcohol to impure ethyl titanite, Et_3TiO_3, which can be further purified by heating at 156°/8—10 mm., whereby some unchanged ethyl titanate distils. The final product is a dark blue, amorphous solid containing about 87·4% of titanite. It reduces aromatic nitro-compounds to amines very readily and aromatic aldehydes to alcohols somewhat more slowly. H. Wren.

Preparation of esters. M. Kotake and Y. Fujita (Bull. Inst. Phys. Chem. Res., Japan, 1928, 7, 734—739).—Nearly quantitative yields of various esters (including those of stearic, succinic, benzoic, malonic, maleic, cinnamic, pyromucic, and salicylic acids) are obtained by heating the acid with a slight excess of alcohol, a quantity of sulphuric acid equivalent to the alcohol used, and anhydrous aluminium sulphate at 100°. Only a 71% yield was obtained in the case of oxalic acid. J. W. Baker.

Action of hydrogen bromide on organic esters at the ordinary pressure. M. Séon (Compt. rend., 1928, **187**, 131—133).—The action of hydrogen bromide under varied conditions of temperature but at atmospheric pressure on amyl formate, amyl salicylate, benzyl acetate, benzyl benzoate, allyl acetate, ethyl acetoacetate, and *cyclo*hexyl acetate leads to the formation of the organic acid and the alkyl, benzyl, or *cyclo*hexyl bromide. Phenyl acetate or benzoate is not decomposed under these conditions.
H. Wren.

Catalytic decomposition of oleic acid. B. M. Marks and H. C. Howard, jun.—See this vol., 968.

Presence of a new fatty acid in a fish oil. H. Marcelet (Compt. rend., 1928, **187**, 145—146).—In addition to stearic, palmitic, and an unidentified acid, m. p. 46—47°, *dorosomic acid*, $C_{17}H_{34}O_2$, m. p. 55°, is isolated from *Dorosoma vasus*, Bloch; the *methyl* ester, m. p. 30°, and the *barium* salt are described. H. Wren.

Ketazines of lævulic acid and lævulhydrazide. C. W. Bennett (J. Amer. Chem. Soc., 1928, **50**, 1747—1748).—Sodium lævulate and hydrazine hydrate in boiling alcohol afford *lævulic acid ketazine*, $C_{10}H_{16}O_4N_2$, m. p. 119—120° (corr.). Lævulhydrazide and hydrazine hydrate give *lævulhydrazide ketazine*, $C_{10}H_{20}O_2N_4$, m. p. 219—220° (corr.). H. Wren.

Structures of convolvulinolic and japalinolic acids. Synthesis of κ-hydroxypentadecoic and κ-hydroxyhexadecoic acids. L. A. Davies and R. Adams (J. Amer. Chem. Soc., 1928, **50**, 1749—1755).—Methyl ι-aldehydododecoate, b. p. 141—143°/4 mm., is converted by magnesium *n*-amyl bromide into *methyl κ-hydroxyhexadecoate*, m. p. 40·5—41·5°, b. p. 183—186°/3 mm. *κ-Hydroxyhexadecoic acid*, m. p. 68—69°, prepared by hydrolysis of the ester, is oxidised by chromic acid in glacial acetic acid to *κ-ketohexadecoic acid*, m. p. 74—75°. Since these acids are obtained also from japalinolic acid by oxidation and subsequent reduction of the keto-acid thus produced, it follows that this acid is *d*-κ-hydroxyhexadecoic acid. Similarly, methyl ι-aldehydododecoate and magnesium *n*-butyl bromide afford *methyl κ-hydroxypentadecoate*, b. p. 166°/2 mm., m. p. 29—32°, from which *κ-hydroxypentadecoic acid*, m. p. 63·5—64°, and *κ-ketopentadecoic acid*, m. p. 70—71°, are derived. Convolvulinolic acid has a structure different from that of κ-hydroxypentadecoic acid. θ-*Ketohexadecoic acid*, m. p. 73·5—74·5°, is described.
H. Wren.

Synthesis of heptane-ϰε-dicarboxylic acid. A. S. Carter (J. Amer. Chem. Soc., 1928, **50**, 1967—1970).—*Ethyl δ-phenoxypropylmalonate*, b. p. 228—

235°/26 mm., is converted successively into δ-*phenoxypropylmalonic acid*, m. p. 72—78° (decomp.), and δ-phenoxyvaleric acid, m. p. 55—56° (*silver* salt). The latter acid is transformed into δ-iodovaleric acid and thence into *ethyl* δ-*iodovalerate*, b. p. 108—118°/20 mm., which is condensed with ethyl ethylsodiomalonate to *ethyl heptane*-αεε-*tricarboxylate*, b. p. 195—200°/20 mm., from which *heptane*-αεε-*tricarboxylic acid*, m. p. 86—88°, and *heptane*-αε-*dicarboxylic acid*, b. p. 218—223°/17 mm., m. p. 41·5—43° (*silver* salt), are derived. H. Wren.

Rotatory dispersion of derivatives of tartaric acid. IV. Propyl and butyl tartrates. P. C. Austin (J.C.S., 1928, 1831—1834).—The rotatory dispersions of di-*n*-propyl, di*iso*propyl, di-*n*-butyl, and di*iso*butyl tartrates have been measured. In each case the rotatory dispersion is both complex and anomalous and is expressed by Drude equations with two terms, the same dispersion constants being used as were determined by Lowry and Abram for the dimethyl (J.C.S., 1915, **107**, 1187) and by Lowry and Cutter for the diethyl ester (*ibid.*, 1922, **121**, 542). No simple relation is found between the rotation constants. The following revised physical data for the esters are given: methyl, m. p. 48° and 61·5° (dimorphous); ethyl, m. p. 18·7°, d_4^{20} 1·2028; *n*-propyl, b. p. 177°/17 mm., d_4^{20} 1·1186; *iso*propyl, b. p. 152°/12 mm., d_4^{20} 1·1136; *n*-butyl, m. p. 21·8°, b. p. 182°/11 mm., d_4^{20} 1·0909; *iso*butyl, m. p. 66°, b. p. 171°/11 mm. J. W. Baker.

Rotatory dispersion of derivatives of tartaric acid. III. Diacetyltartaric acid and its esters. P. C. Austin (J.C.S., 1928, 1825—1831).—Re-examination of the rotatory dispersion of diacetyltartaric acid (cf. Austin and Park, A., 1925, ii, 1028) in ether in place of acetone allows the measurements to be extended further into the ultra-violet, and evidence of its complex dispersion is thus obtained. The rotations in this solvent ($[\alpha]_D$ −17·01°) are much lower than in acetone ($[\alpha]_D$ −24·5°) and it is suggested that the latter may react with the acid to give a bridged compound. The enhanced lævorotations obtained by addition of water to the solution in acetone may be ascribed, as in the case of tartaric acid itself, to an alteration in the equilibrium between two components of opposite sign. The rotatory dispersions of the methyl, ethyl, *n*- and *iso*-propyl, and *n*- and *iso*-butyl esters have been determined. The dispersion of the methyl ester is complex but normal, whilst the other esters exhibit anomalous dispersion. The following revised physical data for esters of diacetyltartaric acid are given: *methyl*, m. p. 118°, $[\alpha]_D$ −17·87° in acetone; ethyl, m. p. 103°, b. p. 179°/17 mm., $[\alpha]_D$ −0·50° in ether; *n*-propyl, m. p. 67°, b. p. 181°/10 mm., d_4^{20} 1·1114, $[\alpha]_D$ (supercooled) +11·02°; *iso*propyl, m. p. 21·5°, b. p. 167°/11 mm., $[\alpha]_D$ +8·63° in ether; *n*-butyl, m. p. 31·4°, b. p. 205°/15 mm., d_4^{20} 1·0823, $[\alpha]_D$ (liquid) +22·20°; *iso*butyl, b. p. 193°/13 mm., d_4^{20} 1·0816, $[\alpha]_D$ (liquid) +67·18°. J. W. Baker.

Oxidation of alcohols to aldehydes and condensation of aldehydes and alcohols to mixed esters. I. S. N. Danilov (Trans. State Inst. Appl. Chem., Moscow, 1927, No. 5, 66—88).—The best results in the catalytic oxidation of amyl and *iso*butyl alcohols were obtained with zinc as catalyst, when 40—70% yields resulted at 580° and a speed of 50—100 g. of alcohol per hr.; with birch charcoal at 320—330°, the yield was 56—57%. Esters were obtained in 94—96% yield by Tischenko's method. Thus, aluminium turnings (0·4 g.) were activated by exposure to a stream of hydrogen chloride, preceded and followed by hydrogen; amyl alcohol (18 c.c.) was added, the metal dissolving in 20 min. Valeraldehyde (100 g.) was then added with cooling and stirring, the mixture being finally heated for 30 min. at 80°, and distilled at 100 mm. Chemical Abstracts.

Catalysis in the conversion of allyl alcohol and acraldehyde into propaldehyde. P. E. Weston and H. Adkins (J. Amer. Chem. Soc., 1928, **50**, 1930—1935).—Study has been made of the behaviour of allyl alcohol and mixtures of it with acraldehyde in presence of a zinc oxide catalyst and of *n*-propyl alcohol and acraldehyde in presence of aluminium oxide. Formation of propaldehyde by passing allyl alcohol over zinc oxide results, at least in part, from the reaction of the alcohol with acraldehyde and not through hydrogenation of acraldehyde or intramolecular rearrangement of allyl alcohol. H. Wren.

Reactions relating to carbohydrates and polysaccharides. XIV. Polymerisation of aldehydes. H. Hibbert, W. F. Gillespie, and R. E. Montonna (J. Amer. Chem. Soc., 1928, **50**, 1950—1955).—Chloral alone or, preferably, in presence of a trace of hydrogen chloride combines with propaldehyde, *iso*butaldehyde, and trimethylacetaldehyde giving substituted *paraldehydes*, $CCl_3{\cdot}CHO,2R{\cdot}CHO$, m. p. 62·5°, 68·5—69°, and 114—115°, respectively, which are stable towards alkali hydroxide but are decomposed by boiling dilute sulphuric acid. Paraldehydes could not be prepared from three different aldehydes or from acetaldol and chloral. H. Wren.

Relations between rotatory power and structure in the sugar group. XVIII. α-Methyl-*d*-lyxoside triacetate. F. P. Phelps and C. S. Hudson (J. Amer. Chem. Soc., 1928, **50**, 2049—2051).—α-*Methyl*-d-*lyxoside triacetate*, m. p. 96°, $[\alpha]_D^{20}$ +30·1° in chloroform, is prepared from α-methyl-*d*-lyxoside and acetic anhydride in warm pyridine. Comparison of its rotation with that of α-methyl-*d*-xyloside triacetate indicates that the lyxoside derivative has a butylene oxide-ring and that crystalline α-lyxose, $[\alpha]_D$ +5·5°, also has this ring structure, since its rotation differs normally from that of α-methyl-*d*-lyxoside. H. Wren.

Acetylmonoses. IV. Two isomeric triacetylmethyl-lyxosides. P. A. Levene and M. L. Wolfrom (J. Biol. Chem., 1928, **78**, 525—533).—α-Methyl-*d*-lyxoside is converted by acetic anhydride in pyridine at 0° into α-*methyl*-d-*lyxoside triacetate*, m. p. 96°, $[\alpha]_D^{20}$ +30·6° in chloroform. α-*d*-Lyxoside tetraacetate is treated with an almost saturated solution of hydrogen bromide in glacial acetic acid giving a syrupy bromo-compound which is treated with methyl alcohol and quinoline; the liberated acid is neutralised by silver carbonate or, preferably, sodium methoxide, whereby *γ-methyl*-d-*lyxoside triacetate*, m. p. 90°, $[\alpha]_D^{20}$ −103·1° in chloroform, is obtained. The syrupy bromoacetyl-lyxose is converted by silver carbonate and methyl alcohol into the α- and γ-methyl-*d*-lyxoside triacetates. The γ-form is very rapidly de-acetylated by treatment with dry methyl alcohol containing 0·1% of hydrogen chloride. H. Wren.

α- and β-Forms of diacetone methylmannoside [methylmannoside di*iso*propylidene ether]. P. A. Levene and G. M. Meyer (J. Biol. Chem., 1928, **78**, 363—367).—α-Methylmannoside is slowly converted by acetone containing 1% of hydrogen chloride into methylmannoside di*iso*propylidene ether, b. p. 105°/0·2 mm., $[\alpha]_D^{20}$ +56·0°, whereas the same product is very rapidly formed from γ-methylmannoside; it is probably identical with the product, $[\alpha]_D^{20}$ +46·6°, obtained by the action of silver oxide and methyl iodide on mannose di*iso*propylidene ether. The specific rotation of the methylmannoside di*iso*propylidene ether prepared from di*iso*propylidenemannose by Freudenberg's method could not be increased beyond −41°. All three products are hydrolysed at the same rate and hence all have the butylene-oxide structure. It follows therefore that the amylene-oxide structure of methylmannoside is changed under the influence of acetone. H. Wren.

Ameliaroside, a new glucoside from *Amelanchier vulgaris*, Moench. M. Bridel, C. Charaux, and G. Rabaté (Compt. rend., 1928, **187**, 56—57).—The *glucoside* crystallises in small prisms containing 4·54% H_2O, m. p. 195°, $[\alpha]_D$ −86·56° (anhydrous). It is hydrolysed by dilute sulphuric acid at 100° or by emulsin to dextrose and *ameliarol*, m. p. 110°, which gives a strong violet coloration with ferric chloride. H. Wren.

Production of furfuraldehyde from oxycellulose. F. W. Klingstedt (Zellstoff u. Papier, 1928, **8**, 471—474).—Distillation of oxycelluloses with hydrochloric acid appears to yield furfuraldehyde when the phloroglucinol method of determination is followed, but the amount has generally been overestimated owing to non-appreciation of the production of hydroxymethylfurfuraldehyde. If the barbituric acid method is used, it appears that cellulose which has not been oxidised too powerfully does not contain groups capable of yielding furfuraldehyde in appreciable amount. The furfuraldehyde, obtained from highly oxidised cellulose in small amount, is derived from non-cellulosic components. H. Wren.

Lignin. II. Fractional extraction of lignin from corn [maize] cobs. M. Phillips (J. Amer. Chem. Soc., 1928, **50**, 1986—1989).—The ground material is subject to a preliminary treatment with boiling alcohol and benzene (1 : 1). Lignin is fractionally extracted by 2% alcoholic sodium hydroxide at the ordinary temperature, by 2% aqueous sodium hydroxide at 100° and 135°, and finally by 4% aqueous sodium hydroxide at 180°, each process being continued until lignin is not further removed before the next process is applied. The lignin is unequally combined with the carbohydrates, part of it being loosely bound possibly in the form of an ester and the remainder more formly retained, probably in ether-like combination. H. Wren.

Effect of the cyano-group on the basicity of aliphatic amines as determined in aqueous and alcoholic solutions. T. D. Stewart and V. Cook (J. Amer. Chem. Soc., 1928, **50**, 1973—1983).—The constants are determined by electrometric titration in water and by colorimetric measurements in alcohol. The basic dissociation constants of α-diethylaminoacetonitrile and of α-diethylaminophenylacetonitrile in water are $1{\cdot}0\times10^{-10}$ and $1{\cdot}7\times10^{-11}$, respectively. In alcoholic solution, the acidic dissociation constants of their salts (chlorides) are $3{\cdot}4\times10^{-5}$ and $5{\cdot}2\times10^{-4}$, respectively, whilst those of α-diethylaminopropionitrile and of α-diethylamino*iso*butyronitrile are $3{\cdot}4\times10^{-5}$ and 2×10^{-6}, respectively. The following compounds are prepared from sodium hydrogen sulphite, diethylamine, potassium cyanide, and the requisite aldehyde or ketone: *α-diethylaminoacetonitrile*, b. p. 62—63°/14 mm.; *α-diethylaminopropionitrile*, b. p. 67—68°/17 mm.; *α-diethylaminophenylacetonitrile*, b. p. 130—131°/11 mm.; *α-diethylamino*iso*butyronitrile*, b. p. 75—77°/23 mm. H. Wren.

Catalytic preparation of methylamine from methyl alcohol and ammonia. T. L. Davis and R. C. Elderfield (J. Amer. Chem. Soc., 1928, **50**, 1786—1789).—Methylamine is formed when methyl alcohol and ammonia are passed over a heated thorium oxide catalyst. Under optimal conditions (325—330°; relative concentration about 0·80—0·83 mol. of ammonia per mol. of methyl alcohol) nearly one third of the methyl alcohol is transformed into methylamine. H. Wren.

Action of organo-magnesium compounds on certain fatty dialkylamides. M. Montagne (Compt. rend., 1928, **187**, 128—130).—The action of butyl bromide or iodide on a mixture of butyrdiethylamide and magnesium methyl iodide yields β-diethylamino-β-methylpentane and *δ-diethylamino-δ-methylnonane*, b. p. 128—129°/20 mm. (*picrate*, m. p. 78—79°; *chloroaurate*, m. p. 54°); the *hydrochloride* of the latter is decomposed by heat into diethylammonium chloride and a *hydrocarbon*, $C_3H_7{\cdot}CMe{:}CH{\cdot}C_5H_9$ or $CHEt{:}CMe{\cdot}CH_2{\cdot}C_5H_9$, b. p. 161—164°. If benzyl chloride is employed, the products are β-diethylamino-β-methylpentane and *γ-diethylamino-α-phenyl-γ-methylhexane*, b. p. 163°/10 mm. (*picrate*, m. p. 99°; *chloroaurate*, m. p. 101°). H. Wren.

Additive compounds of cadmium halides with hexamethylenetetramine. VI. G. Scagliarini and E. Brasi (Atti R. Accad. Lincei, 1928, [vi], **7**, 509—511).—In order to trace the influence of the solvent particularly with respect to the dielectric constant the formation of additive *compounds* between cadmium halides and hexamethylenetetramine has been examined in water and in acetone. Dilute aqueous solutions of cadmium halides when mixed with a dilute aqueous solution of hexamethylenetetramine leads to the precipitation of the crystalline substances $2CdCl_2,C_6H_{12}N_4$, $CdBr_2,2C_6H_{12}N_4$, and $CdI_2,C_6H_{12}N_4,8H_2O$. Gradual addition of a concentrated acetone solution of the base to a concentrated acetone solution of cadmium chloride leads to the formation of the complex $CdCl_2,C_6H_{12}N_4$. A similar procedure in the case of cadmium bromide furnishes the compound $3CdBr_2,2C_6H_{12}N_4$, whilst the addition of the halide solution to the base gives rise to the substance $CdBr_2,C_6H_{12}N_4$. From cadmium iodide only one substance is formed, viz., $2CdI_2,C_6H_{12}N_4$. R. W. LUNT.

Action of thiocyanogen on *ON*-disubstituted hydroxylamines and primary amines. L. W. JONES and E. E. FLECK (J. Amer. Chem. Soc., 1928, **50**, 2018—2028).—N-*Thiocyano*-ON-*diethylhydroxylamine*, b. p. 45—46°/2 mm., prepared by the action of thiocyanogen on *ON*-diethylhydroxylamine in ether, is hydrolysed by 2% hydrochloric acid at 0° to hydrocyanic, thiocyanic, and sulphuric acids and ethoxyethylammonium chloride (identified as β-ethoxy-α-phenyl-β-ethylcarbamide, m. p. 63°), and by 2% potassium hydroxide to ammonia, ethylamine, acetaldehyde, and potassium thiosulphate. *Ethyl* ON-*carbethoxydibenzylhydroxamate*, b. p. 200—203°/7 mm., prepared from carbethoxyhydroxamic acid, benzyl chloride, and potassium hydroxide, is hydrolysed to ON-*dibenzylhydroxylamine*, b. p. 145—146°/3 mm., which, with thiocyanogen, affords N-*thiocyano*-ON-*dibenzylhydroxylamine*, m. p. 91°, and *benzyloxybenzylammonium thiocyanate*, m. p. 50—52°. The hydroxylamine is hydrolysed in exactly the same manner as the corresponding diethyl compound. At an elevated temperature *ON*-disubstituted hydroxylamines are hydrolysed by alkali hydroxide to the corresponding aldehyde and amine.

Thiocyanotriphenylmethylamine, $CPh_3{\cdot}NH{\cdot}SCN$, m. p. 142° (*thiocyanate*, m. p. 173°), is prepared from thiocyanogen and triphenylmethylamine in ether. It suffers rearrangement when heated with calcium oxide at 440—450° yielding benzophenoneanil (identified by hydrolysis to aniline and benzophenone). Thiocyanobenzylamine could not be obtained homogeneous. The preparation of *α-benzyloxy-α-benzylcarbamide*, m. p. 98—99°, and *α-benzyloxy-α-benzylthiocarbamide*, m. p. 94—95°, is recorded. H. WREN.

Action of nitrous acid on amino-compounds. II. Aliphatic amino-acids. T. W. J. TAYLOR (J.C.S., 1928, 1897—1906).—The velocity of reaction of nitrous acid with glycine and α- and β-alanine has been measured in dilute aqueous solution at 25°, the reaction being followed by determination of the amino-acid by a modification of Sörensen's formaldehyde titration method (A., 1908, i, 115). The reaction velocity with 1 equivalent of nitrous acid is diminished by addition of mineral acids or neutral salts. The hydroxy-acid formed in the reaction has no negative autocatalytic effect. The reaction velocity was measured in 0·05*N*- and 0·025*N*-solution in the case of glycine and α-alanine, and in 0·05*N*- and 0·04*N*-solution with β-alanine where the reaction is much slower. In every case the reaction is approximately of the third order. Doubling the concentration of nitrous acid increases the velocity to a greater extent than does doubling that of the amino-acid. Hence two of the molecular species involved must be nitrous acid, and the third some form of the amino-acid. The latter is present in two forms, $NH_3^+{\cdot}RCO_2^-$ (A^{+-}) and $NH_3^+{\cdot}RCO_2H$ (A^+), and mathematical analysis of the kinetics of the reaction shows that the ratio of the concentrations of these two forms is almost independent of the concentration, the values in 0·05*N*- and 0·025*N*-solution being for glycine, 0·786 and 0·800, α-alanine, 0·721 and 0·718, and for β-alanine 0·444 and 0·444, respectively. The reaction velocity was measured in the presence of 0·05*N*- and 0·1*N*-sulphuric acid, the presence of which lowers the reaction velocity, and would increase the concentration of A^+ and decrease the concentration of the nitrite ion and A^{+-}, and the velocity coefficients were calculated with various assumptions regarding the molecular species involved in the reaction. Agreement between the various experiments is reached only if the reacting species are (A^{+-}) and HNO_2, and the reaction velocity is thus proportional to the product $[A^{+-}][HNO_2]^2$. The apparent difference in the speeds of reaction in the three cases studied arises mainly from the difference in the acid dissociation constants; the smaller is the value of these, the smaller is the concentration of the form A^{+-} present. J. W. BAKER.

Preparation of *d*-arginine monohydrochloride. G. J. COX (J. Biol. Chem., 1928, **78**, 475—479).—Gelatin is hydrolysed by concentrated hydrochloric acid and the solution is concentrated to a thick syrup under reduced pressure. The residue is dissolved in water, neutralised with concentrated sodium hydroxide to Congo-red, and the arginine is precipitated as the flavianate. The precipitate is heated with concentrated hydrochloric acid, separated from flavianic acid, and again concentrated to a thick syrup in a vacuum. The syrup is dissolved in 95% alcohol and the solution cooled to cause the separation of residual flavianic acid as the arginine salt. After removal of the latter, the solution is treated with aniline, which causes the separation of *d*-arginine monohydrochloride. The latter substance is purified by crystallisation from a mixture of alcohol and water; it has m. p. 222° (corr.). H. WREN.

Action of picric acid on glycylglycine. A. MOREL, P. PRECEPTIS, and A. GALY (Compt. rend., 1928, **187**, 173—174).—Glycylglycine affords a crystalline monopicrate when its aqueous solution is mixed with picric acid and evaporated to dryness in a vacuum at the ordinary temperature; the residue is washed with ether and crystallised by slow evaporation of its aqueous solution. Alternatively, glycylglycine and picric acid are dissolved in aqueous barium hydroxide, the mixture is boiled, and the barium quantitatively removed by sulphuric acid; after removal of barium sulphate, the filtrate is slowly concentrated. Under the first set of conditions, glycine affords the monopicrate of diglycine. H. WREN.

Reciprocal action of picric acid and *cyclo*-glycylglycine. A. MOREL and P. PRECEPTIS (Compt. rend., 1928, **187**, 236—239).—In acid solution, the monopicrate of monoglycylglycine is obtained from the substances mentioned in the title. In faintly alkaline solution the same substance is obtained but reduction of picric acid also occurs. H. WREN.

Carbonic acid azides. C. V. HART (J. Amer. Chem. Soc., 1928, **50**, 1922—1930).—*Dicyanodiazide*, $CN{\cdot}N{:}C(N_3)_2$, m. p. 40·3° (corr.), prepared by the action of cyanogen bromide on an aqueous solution of sodium azide (previously regarded as carbon pernitride), is converted by ammonia into ammonium azide and *dicyanoamidoazide*, m. p. 151—152° (decomp.). It is hydrolysed by boiling water to azoimide and cyanamide, but reaction is not quantitative owing to formation of 5-aminotetrazole; if sodium hydroxide is used, sodium azide and sodium cyanamide are quantitatively formed. Dicyanodiazide is reduced by hydrogen sulphide to dicyanodiamide, m. p. 207·4°, which is similarly produced from dicyanoamidoazide. The ability of a substance to form sodium azide with sodium hydroxide and to yield an amine, sulphur, and nitrogen when reduced with hydrogen sulphide is regarded as specific evidence of the presence of azide groups, since these reactions are not shown by the isomeric tetrazoles. Treatment of an alcoholic solution of dicyanodiazide with aniline causes production of *dicyanophenylamidoazide*, decomp. 145° (*sodium* salt), reduced by hydrogen sulphide to phenyldicyanodiamide, m. p. 195—196° (probably identical with phenylcyanoguanidine). With α-naphthylamine, dicyanodiazide affords *dicyano-α-naphthylamidoazide* (*sodium* salt). Unexpectedly, the action of cyanogen bromide on the sodium salt of 5-aminotetrazole yields dicyanoamidoazide. Cyanurtriazide, $C_3N_3(N_3)_3$, is hydrolysed by sodium hydroxide to sodium azide and cyanuric acid and reduced by hydrogen sulphide to melamine, thus establishing the complete absence of tetrazole groups. *Cyanuramidodiazide*, $C_3N_3(NH_2)(N_3)_2$, decomp. above 200°, is formed by the action of ammonia on cyanurtriazide in ether. *Cyanuric dichloride azide*, m. p. 85°, is prepared from cyanuric trichloride and sodium azide. H. Wren.

Preparation of cyanogen by the wet method. C. Noir and Tching-Datchong (Compt. rend., 1928, **187**, 126—128).—The following procedure is adopted in analysis of the gas evolved by the action of potassium cyanide on copper sulphate. The gases are absorbed in 0·5*N*-potassium hydroxide and cyanogen is determined by addition of an excess of silver nitrate, removal of silver cyanide after acidification with nitric acid, and measurement of the residual silver. Carbon dioxide is determined by passing a known volume of gas into barium hydroxide and titration of the precipitated barium carbonate. Determination of hydrocyanic acid depends on passage of the gases into an excess of silver nitrate, removal of silver cyanide, and measurement of residual silver. The gas is found to contain 78% of cyanogen, 20% of carbon dioxide, and 1—2% of hydrocyanic acid. Carbon dioxide appears to be formed by hydrolysis of the cyanate. H. Wren.

Luminescence of aliphatic Grignard compounds. R. T. Dufford (J. Amer. Chem. Soc., 1928, **50**, 1822—1824).—Magnesium methyl, ethyl, propyl, and butyl bromides all emit faint light when oxidised. The effects are observed only at dilutions considerably greater than those used with magnesium aryl halides. H. Wren.

Preparation of mercury dimethyl. K. Fuchs (J. pr. Chem., 1928, [ii], **119**, 209—210).—A mixture of acid-free methyl sulphate (1 mol.), methyl acetate, and 0·5% sodium amalgam (1 mol. Na) is shaken in a pressure flask, at first cautiously, until the temperature, which rises to 60—70°, has fallen to 15°. The yield of pure mercury dimethyl, b. p. 91·5—92·5°/745 mm., is 60—65%, calculated on the sodium used. Methyl acetoacetate cannot replace the methyl acetate as catalyst. Addition of mercuric chloride and a corresponding excess of methyl sulphate gives only a 55% yield of mercury dimethyl, accompanied by some mercury methyl chloride. Ethyl sulphate has no advantage over ethyl bromide for mercury diethyl. C. Hollins.

Use of platinum oxide–platinum-black in the catalytic reduction of aromatic hydrocarbons. XVII. R. Adams and J. R. Marshall (J. Amer. Chem. Soc., 1928, **50**, 1970—1973).—Excellent results are recorded for the hydrogenation of the following aromatic compounds in presence of the catalyst and glacial acetic acid at 25—30° and 2—3 atm.: benzene, toluene, ethylbenzene, *m*-xylene, mixed xylenes, mesitylene, cymene, di- and tri-phenylmethane, αα-diphenylethane, dibenzyl, phenylacetic and β-phenylpropionic acids. H. Wren.

Tetraphenyldi*tert.*-butylethane. J. B. Conant and N. M. Bigelow (J. Amer. Chem. Soc., 1928, **50**, 2041—2049).—Diphenyl*tert.*-butylmethyl chloride, m. p. 71—72°, is rapidly converted by 40% sodium amalgam in ether in an atmosphere of nitrogen into the brick-red *sodium diphenyl*tert.*-butylmethyl*, the constitution of which is established by its transformation into *diphenyl*tert.*-butylacetic acid*, m. p. 160° (p-*nitrobenzyl* ester, m. p. 77°). The sodium salt is transformed by tetramethylethylene dibromide into *tetraphenyldi*tert.*-butylethane*, m. p. 138—141° (in an atmosphere of nitrogen), from which the sodium compound is readily re-formed. The hydrocarbon rapidly absorbs oxygen in solution at 25°, but a peroxide could not be isolated. On heating a dilute solution to 55°, a reversible colour change indicative of dissociation appears. When heated for a few minutes in solution at 100° in absence of air, it disproportionates completely. The effect of the tertiary alkyl group in promoting dissociation of the C–C linking is thus similar to that of secondary groups in the dixanthyl series. If an insufficient amount of sodium–potassium alloy is employed in place of sodium amalgam in the preparation of *potassium diphenyl*tert.*-butylmethyl*, the yield is much lowered and about half the chloride is converted into a *hydrocarbon*, $C_{34}H_{38}$, m. p. 145°, isomeric with tetraphenyldi*tert.*-butylethane; this substance does not react with oxygen or with sodium–potassium alloy. Treatment of the isomeric diphenyl*tert.*-butylmethyl chloride, m. p. 103—106°, or of γγ-diphenyl-β-methyl-Δ^{α}-butene with sodium–potassium alloy in ether gives a red metallic *derivative* differing from the sodium compound described above, since it is converted by carbon dioxide into an *acid*, $C_{18}H_{20}O_2$, m. p. 218—224° (decomp.) (non-crystalline p-*nitrobenzyl* ester), and by tetramethylethylene dibromide into an oil which does not absorb oxygen. H. Wren.

Effects induced by the phenyl group. I. Addition of polar reagents to styrene and the behaviour of the halogenated benzenes. F. Ashworth and N. Burkhardt (J.C.S., 1928, 1791—1802).—The interaction of styrene with hydrogen bromide, ammonium hydrogen sulphite, and thiophenol, and of α- and β-bromoethylbenzenes and αβ-dibromoethylbenzene with aqueous-alcoholic potassium hydroxide has been studied. Addition of hydrogen bromide and ammonium hydrogen sulphite to styrene occurs in accordance with the Markownikoff rule and requires negative free affinity on the ω-carbon atom in styrene, the sole products being, respectively, α-bromoethylbenzene and, after treatment with barium hydroxide, *barium α-phenylethanesulphonate* (+H_2O and anhydrous). The latter was identical with the product obtained by the action of ammonium sulphite on α-bromoethylbenzene, and was different from *barium β-phenylethanesulphonate* (+H_2O and anhydrous), similarly prepared from β-bromoethylbenzene. Posner's conclusion (A., 1905, i, 279) that the addition of thiophenol to styrene takes place quantitatively in the opposite sense to that of hydrobromic acid is confirmed, since the product is phenyl β-phenylethyl sulphide, b. p. 188—189°/15 mm., n_D 1·6082, contaminated, as measurements of its refractive index show, with less than 2% of phenyl α-phenylethyl sulphide, b. p. 163—164°/15 mm., n_D 1·6042. By oxidation the reaction product yields only phenyl β-phenylethyl sulphone identical with that obtained by the action of sodium benzenesulphinate on β-bromoethylbenzene. The reaction is accompanied by a 10% contraction and can thus be followed dilatometrically. It is greatly accelerated by the action of light, the increase in the rate of addition produced by exposure to sunlight continuing for some time after the reaction mixture is returned to diffuse daylight. Piperidine is a powerful retarding agent. Cryoscopic measurements of thiophenol, styrene, and mixtures of these in benzene show that no association takes place. By the action of boiling aqueous-alcoholic potassium hydroxide solution (0·4N) α-bromoethylbenzene is converted quantitatively into phenylmethylcarbinol; the β-compound yields only styrene, whilst styrene dibromide yields only α-bromostyrene. The conjugative electronic displacements which may occur in styrene in its various reactions are discussed. J. W. Baker.

Derivatives of *n*-butylbenzene. R. R. Read and D. B. Mullen (J. Amer. Chem. Soc., 1928, **50**, 1763—1765).—*n*-Butylbenzene is converted by nitration in presence of sulphuric acid into a mixture of o-*nitro*-n-*butylbenzene*, b. p. 131—133°/15 mm., d_4^{20} 1·071, and p-*nitro*-n-*butylbenzene*, b. p. 143—145°/15 mm., d_4^{20} 1·065. o-n-*Butylaniline*, b. p. 122—125°/12 mm., d_4^{20} 0·953 (*hydrochloride*, m. p. 137°), is prepared in the usual manner. o-n-*Butylphenol*, b. p. 113—115°/14 mm., d_4^{20} 0·975, and p-n-*butylphenyl* p-*nitrobenzoate*, m. p. 67—68°, are described. m-n-*Butylphenol* has b. p. 247—249°/758 mm., d_4^{23} 0·974. H. Wren.

Dichloro-*o*-xylenes. L. E. Hinkel, E. E. Ayling, and L. C. Bevan (J.C.S., 1928, 1874—1878).—Dichlorination of pure *o*-xylene with gaseous chlorine in presence of iron filings at −10° yields mainly 4 : 5-dichloro- (I), m. p. 76°, b. p. 240° (corr.), and 3 : 4-*dichloro-* (II), m. p. 9°, b. p. 234° (corr.), together with a small quantity of 3 : 6-*dichloro-* (III), m. p. 68°, b. p. 227° (corr.), -o-*xylenes*. All on further chlorination yield the same tetrachloro-*o*-xylene, m. p. 227°. Oxidation of (I) yields 4 : 5-dichlorophthalic acid (Villiger, A., 1909, i, 930). Nitration with a mixture of fuming nitric and acetic acids converts it into 4 : 5-*dichloro*-3-*nitro*-o-*xylene*, m. p. 117°, which is reduced by iron and glacial acetic acid to 4 : 5-*dichloro*-3-o-*xylidine*, m. p. 88° (*acetyl* derivative, m. p. 197°). This is converted by the Sandmeyer reaction into a mixture of 3 : 4 : 5-trichloro-*o*-xylene and tetrachloro-*o*-xylene. When heated for 10 min. with nitric and sulphuric acids, (I) yields 4 : 5-*dichloro*-3 : 6-*dinitro*-o-*xylene*, m. p. 210°, which by reduction in alcoholic solution with sodium hydrosulphite yields the *diamine*, m. p. 186°. Nitration of (II) yields 3 : 4-*dichloro*-5-*nitro*-o-*xylene*, m. p. 78° (together with a little of the 6-nitro-isomeride), dinitration yielding 3 : 4-*dichloro*-5 : 6-*dinitro*-o-*xylene*, m. p. 172°. Reduction of the 5-nitro-compound yields 5 : 6-*dichloro*-o-4-*xylidine*, m. p. 63° (*acetyl* derivative, m. p. 147°), whilst from the dinitro-compound is obtained 3 : 4-*dichloro*-5 : 6-*diamino*-o-*xylene*, m. p. 176°, which reacts with phenanthraquinone. Nitration of (III) yields 3 : 6-*dichloro*-4-*nitro*-o-*xylene*, m. p. 220°. Nitration of 3 : 5-dichloro-*o*-xylene (Crossley, J.C.S., 1902, 81, 1533) with a mixture of fuming nitric and glacial acetic acids on a water-bath yields 3 : 5-*dichloro*-4-*nitro*-o-*xylene*, m. p. 92° (contaminated with a little 6-nitro-isomeride), which is reduced to 3 : 5-dichloro-4-*o*-xylidine, m. p. 47·5° [acetyl derivative, m. p. 196°; Crossley (*loc. cit.*) gives 44·5° and 186°, respectively]. J. W. Baker.

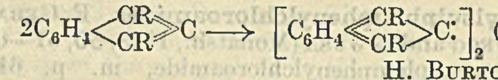
M. p. of *m*-dinitrobenzene. F. McCamish and A. Salathe (J. Amer. Chem. Soc., 1928, **50**, 1785).—The value m. p. 89·85° is determined. H. Wren.

Arylsulphonphenylchloroamides. E. Gebauer-Fülnegg and E. Jusa (Monatsh., 1928, **50**, 61—67).—Benzenesulphonphenylchloroamide, m. p. 61°, is stable when pure and acid-free, but readily changes into benzenesulphon-*p*-chloroanilide, m. p. 121°, in presence of traces of acid. The activity of the halogen atom towards reagents is governed by the relative speed of this isomerisation. Electrolysis of the chloroamide in solution in liquid sulphur dioxide leads to a little benzenesulphonanilide in the cathode chamber and benzenesulphon-*p*-chloroanilide in both cathode and anode chambers. Pyridine, potassium hydroxide, and sodium methoxide give in that order increasing amounts of benzenesulphon-*o*-chloroanilide and diminished quantities of the above two products; sodium in dry ether gives exclusively the *o*-chloroanilide. On the other hand, the isomerisation is completely excluded when the chloroamide is treated with ammonia or with mercury, benzenesulphonanilide being the only product. Sodium iodide yields benzenesulphon-*p*-iodoanilide, sodium nitrite the *p*-nitroanilide, and sodium cyanide a mixture of products. With aluminium chloride isomerisation, but no condensation, occurs. C. Hollins.

Synthesis of *meso*-alkyl and *meso*-aryl anthracene derivatives. IV. E. de B. Barnett and J. L. Wiltshire (J.C.S., 1928, 1822—1825).—Addition of zinc dust and a few c.c. of copper sulphate solution to a solution of 4-chloro-*o*-benzoylbenzoic acid in ammonia (*d* 0·880) yields 4-*chlorodiphenylmethane-2′-carboxylic acid*, m. p. 132°, which is converted by cold concentrated sulphuric acid into 2-*chloro*-9-*anthrone*, m. p. 155°, from which 2-*chloro*-9-*anthranyl acetate*, m. p. 143°, is obtained by the acetic anhydride–pyridine method (Barnett and Matthews, J.C.S., 1923, **123**, 389). 3-*Chloro*-9-*anthranyl acetate*, m. p. 146° (depressing m. p. of 2-chloro-compound), is prepared similarly. By the action of the Grignard reagent on 2-chloro-9-anthrone are obtained 2-*chloro*-9-*methyl*-, m. p. 184°, 2-*chloro*-9-*ethyl*-, m. p. 79° (which by bromination yields 2-*chloro*-10-*bromo*-9-*ethylanthracene*, m. p. 128°), 2-*chloro*-9-n-*propyl*-, m. p. 82°, or 2-*chloro*-9-*benzyl*-, m. p. 132° [which by bromination yields 2-*chloro*-10-*bromo*-9-*benzylanthracene*, m. p. 167° (*dibromide*, decomp. 150°)], *anthracene*. Good yields could be obtained only with magnesium ethyl bromide and magnesium benzyl chloride. J. W. Baker.

Coloured rubrene hydrocarbons. C. Moureu, C. Dufraisse, and A. Willemart (Compt. rend., 1928, **187**, 266).—The preparation of a *dimethylrubrene*, m. p. 315°, from *p*-tolylacetylene and benzophenone and of a *dibenzorubrene*, m. p. 280°, from β-naphthylacetylene and benzophenone is indicated. H. Wren.

Coloured rubrene hydrocarbons. A. Willemart (Compt. rend., 1928, **187**, 385—387; cf. A., 1926, 945, and preceding abstract).—The formation of rubrene hydrocarbons (II) from chloro-compounds of the type CR‴:C·CR′R″Cl is explained by elimination of 1 mol. of hydrogen chloride from the tautomeric allene derivative CR′R″:C:CR‴Cl, and subsequent production of a dimeride from the unstable cyclic intermediate (I).

(I.)

$$2C_6H_4{<}\genfrac{}{}{0pt}{}{CR}{CR}{\gg}C \longrightarrow \left[C_6H_4{\ll}\genfrac{}{}{0pt}{}{CR}{CR}{>}C\colon\right]_2$$
(II.)

H. Burton.

Electrolytic oxidation of aniline. J. Sládek. See this vol., 969.

Condensation of phenylenediamines with acetanilide. Salts of tolylphenylethenylamidines. H. Becker (Rocz. Chem., 1928, **8**, 242—249).—Diphenylethenylamidine (*hydrochloride*, m. p. 218°; *hydrobromide*, m. p. 200°) is prepared by condensing acetanilide with aniline in the presence of phosphoryl chloride. Using *m*-phenylenediamine the product is m-*phenylenedi*(*phenylethenylamidine*), m. p. 213° (*hydrochloride*, m. p. 275°). When *o*-phenylenediamine was used, no condensation product was obtained. The *hydrochlorides* of *o*- and *p*-tolylphenylethenylamidine melt respectively at 154—156° and 194°, and the *hydrobromide* of the corresponding *m*-compound at 152°. R. Truszkowski.

Action of aromatic sulphonyl chlorides on tertiary bases. A. Wahl (Rev. gén. Mat. Col., 1928, **32**, 176—177; cf. A., 1902, i, 822; 1905, i, 194; this vol., 878).—Toluene *o*- and *p*-, and probably all, sulphonyl chlorides react with dimethylaniline, giving crystal-violet in small yield, tetramethyldiaminodiphenylmethane, and probably 4′-dimethylamino-4-methyldiphenylsulphone. Methyl-violet is not produced (cf. A., 1880, 75, 108). Similarly, diethylaniline and methyldiphenylamine yield violet and blue dyes, respectively. A. McGookin.

***ar*-α-Substituted hydrindenes.** E. Goth (Ber., 1928, **61**, [*B*], 1459—1460).—*ar*-1-Aminohydrindene, its acetyl and benzoyl derivatives have m. p. −3°, 126°, and 136°, respectively. 1-Hydroxyhydrindene melts at 47—51°. H. Wren.

Syntheses in the diphenyl series. L. E. Hinkel and D. H. Hey (J.C.S., 1928, 1838—1840).—The decomposition products of 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one (this vol., 760) have now been proved to be 5-bromo- and 4 : 5-dibromo-3-hydroxydiphenyl, respectively, by synthesis of these compounds from 5-bromo-3-nitro-4-aminodiphenyl (I) [m. p. (pure) 100°; cf. Scarborough and Waters, A., 1927, 656]. Acetylation yields 5-bromo-3-nitro-4-acetamidodiphenyl, identical with the compound described by Bell and Robinson (A., 1927, 657). Reduction of 5-bromo-3-nitrodiphenyl yields 5-*bromo*-3-*aminodiphenyl*, m. p. 88° (*acetyl* derivative, m. p. 140°), converted by diazotisation into 5-bromo-3-hydroxydiphenyl, which yields a benzoyl derivative identical with that prepared from one of the decomposition products of 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one. Diazotisation of (I) in hydrobromic acid solution yielded no trace of 4 : 5-dibromo-3-nitrodiphenyl (cf. Crossley, J.C.S., 1904, **85**, 278). 5 : 4′-Dibromo-3-nitro-4-aminodiphenyl (II), m. p. 154° (cf. Scarborough and Waters, *loc. cit.*), is obtained. Acetylation of (II) yields 5 : 4′-dibromo-3-nitro-4-acetamidodiphenyl, identical with the compound described by Bell and Robinson (*loc. cit.*) as (5? : 4′)-dibromo-3-nitro-4-acetamidodiphenyl. Reduction of (II) gives 5 : 4′-*dibromo*-3 : 4-*diaminodiphenyl*, m. p. 120° (*dibenzoyl* derivative, m. p. 278°). Diazotised 5-bromo-3-nitro-4-aminodiphenyl reacts with a solution of cuprous bromide in hydrobromic acid, giving 4 : 5-*dibromo*-3-*nitrodiphenyl*, m. p. 125°. Reduction of this compound yields 4 : 5-*dibromo*-3-*aminodiphenyl* (*acetyl* derivative, m. p. 177°), which is converted into 4 : 5-dibromo-3-hydroxydiphenyl identical with the second decomposition product from 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one. M. Clark.

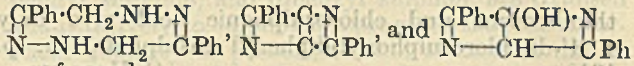
Azochromophores. I and II. J. S. P. Blumberger (Chem. Weekblad, 1928, **25**, 282—286, 315—318).—An examination of the effect of the hydroxyl, amino-, and methyl groups as substituents in azo-dyes on the absorption spectra has been made by collecting examples and data from the literature. The effects are explained on the author's theory of the deformation of the valency-electron fields as the result of substitution. Substituents are divided into two classes. The first, which includes the hydroxyl and amino-groups, repel the electrons of the chromophore when introduced in the *ortho*- and *para*-positions, the effect being reversed when *meta*-substitution occurs. With the second class, the opposite effects are produced. The methyl group is classed as neutral. The effects of the halogen, nitro-, aldehydo-, carboxyl, and sulphonic acid groups are considered. The halogens also repel the valency electrons of the chromophore when present in the *ortho*- and *para*-positions. S. I. Levy.

Copper compounds of some aminoazo- and hydroxyazo-derivatives. A. Cremonini (Gazzetta, 1928, **58**, 372—379).—1-Benzeneazo-2-benzylnaphthylamine (this vol., 629) gives with ammoniacal copper sulphate a *copper* derivative, as does the corresponding 1-*p*-nitrobenzeneazo-compound: definite compounds are, however, not obtained.

The copper derivatives of benzeneazo-β-naphthylamine (cf. Charrier and Beretta, A., 1927, 237) and benzeneazo-β-naphthol (cf. Schaposchnikoff and Svientoslavski, A., 1905, i, 161) are reinvestigated. Whereas Charrier obtained a red compound, m. p. 130°, *copper bisbenzeneazo-β-naphthylamine*, green, m. p. 174°, is now obtained. This when heated under reflux at 250—260° yields aniline, ammonia, αβ-naphthylenediamine, and 2-phenyl-αβ-naphthotriazole, with copper and copper oxide. *Copper bisbenzeneazo-β-naphthol*, brown, m. p. 288°, is prepared. These compounds are violently oxidised by nitric acid; when treated with hydrochloric acid they yield cupric chloride and the parent substance, with no hydrogen or reduced product, which shows that the formulæ ascribed by Charrier (*loc. cit.*; hydrogen remains unreplaced) are erroneous. The compounds are considered to have tautomeric forms, in which copper either (*a*) replaces hydrogen in the amino- or hydroxyl group, and is co-ordinately attached to the nitrogen atom adjacent to the phenyl group, or (*b*) is attached in the reverse manner to the *o*-quinonoid tautomeride: in each form a 6-membered ring is present. Attempts to determine the number of active hydrogen atoms (cf. Ciusa, A., 1920, i, 665) were unsuccessful. E. W. Wignall.

Coupling of diazonium salts in the side-chains of unsaturated compounds. I. A. Quilico and (Signa.) M. Freri (Gazzetta, 1928, **58**, 380—390).—*p*-Nitrobenzenediazonium sulphate dissolved in acetic acid, or, better, suspended in alcohol, reacts with anethole to give anisaldehyde-*p*-nitrophenylhydrazone, m. p. 161°, identified by oxidation and by synthesis, and with *iso*safrole to give *piperonal*-p-*nitrophenylhydrazone*, m. p. 199—200°, also oxidised and synthesised (m. p. 201°); in each reaction a small amount of a red *substance*, m. p. 222—223° (decomp.), regarded as a decomposition product of the diazo-compound, is obtained. Using 2 : 4-dinitrobenzenediazonium sulphate, *anisaldehyde-* and *piperonal*-2 : 4-*dinitrophenylhydrazones*, m. p. 243° and 265° (decomp.), respectively, are obtained, and are also synthesised. From *iso*apiole, *apiolaldehyde*-p-*nitrophenylhydrazone*, m. p. 228—229°, is prepared. It is suggested that the diazo-compound forms an unstable product by addition at the double linking, followed by loss of acetaldehyde; substances with side-chains of the allyl type (*e.g.*, safrole) give uncertain or negative results. E. W. Wignall.

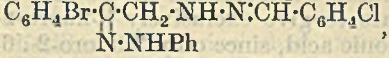
Phenacylhydrazine. M. Busch and W. Foerst [with W. Stengel] (J. pr. Chem., 1928, [ii], **119**, 287—302).—*Phenacylhydrazine*, $CH_2Bz{\cdot}NH{\cdot}NH_2$, m. p. 85—86° (decomp.) [*oxalate*, m. p. 150° (decomp.)], is obtained by condensing phenacyl bromide with hydrazine hydrate in absolute alcohol at −5° and removing hydrazine hydrobromide by ice-water. It is very reactive, and when heated in alcoholic solution loses ammonia, forming 2 : 5-diphenyl-3 : 4-dihydro-1 : 4 : 3-pyrazone (cf. Gastaldi, A., 1921, i, 604). It is suggested that the intermediate products



$$\begin{array}{l}\mathrm{CPh{\cdot}CH_2{\cdot}NH{\cdot}N}\\ \mathrm{N{-}NH{\cdot}CH_2{-}CPh}\end{array},\quad \begin{array}{l}\mathrm{CPh{\cdot}C{\cdot}N}\\ \mathrm{N{-}C{\cdot}CPh}\end{array},\ \text{and}\ \begin{array}{l}\mathrm{CPh{\cdot}C(OH){\cdot}N}\\ \mathrm{N{-}CH{-}CPh}\end{array}$$

are formed.

By the action of acetic acid and anhydride, *diacetylphenacylhydrazine*, m. p. 123°, is prepared; and, with the appropriate aldehydes, o- and m-*nitrobenzaldehyde*-, m. p. 156° (decomp.) and 146—147°, respectively, and *salicylaldehyde*-, m. p. 110° (decomp.), *phenacylhydrazones*, in imperfect yield, owing to decomposition of the reagent. Similarly are prepared: p-*bromophenacylhydrazine*, m. p. 135—136° (decomp.) (*hydrochloride*, decomp. from 170°, sintering 210°; *perchlorate*, m. p. 270°; *oxalate*), decomposing in alcohol to 2 : 5-*di*-p-*bromophenyl*-3 : 4-*dihydro*-1 : 4 : 3-*pyrazone*, m. p. 248—249°, with a *substance* of similar nitrogen content, m. p. 252—254°; and *salicylaldehyde*-, m. p. 125° (decomp.), m-*nitrobenzaldehyde*-, m. p. 136° (decomp.), and p-*chlorobenzaldehyde*-, darkens 128°, m. p. 134° (decomp.), p-*bromophenacylhydrazones*. The last substance reacts at its carbonyl group with phenylhydrazine to give its *phenylhydrazone*, m. p. 214° (decomp.), to which the *syn*-formula,



$$\begin{array}{l}\mathrm{C_6H_4Br{\cdot}C{\cdot}CH_2{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4Cl}\\ \qquad\quad\mathrm{N{\cdot}NHPh}\end{array}$$

, is given, since it combines with formaldehyde, acetaldehyde, or benzaldehyde, in alcoholic solution under the influence of a trace of hydrogen chloride, to furnish, respectively, 1-p-*chlorobenzylideneamino*-3-*phenyl*-, m. p. 180° (decomp.), -3-*phenyl*-2-*methyl*-, m. p. 166°, and -2 : 3-*diphenyl*-, m. p. 163—164°, -5-p-*bromophenyl*-1 : 2 : 3 : 6-*tetrahydro*-1 : 3 : 4-*triazines*.

m-*Nitrophenacylhydrazine*, m. p. 100° (decomp.), decomposes readily, *e.g.*, when an attempt is made to combine it with *p*-chlorobenzaldehyde, giving only bis-*p*-chlorobenzylideneazine. E. W. Wignall.

Preparation of phenyl and tolyl oxalates. J. Mikšić and Z. Pinterović (J. pr. Chem., 1928, [ii], **119**, 231—234).—Aryl oxalates are readily obtained pure by the action of oxalyl chloride (1 mol.) on phenols (2 mols.) in dry ether in presence of sodium or potassium, cooling in a freezing-mixture being necessary to control the vigorous reaction which begins after a few hrs. with *m*- and *p*-cresols, or after 24 hrs. with *o*-cresol and phenol. C. Hollins.

Preparation of derivatives of phenolsulphonyl chloride. E. Gebauer-Fülnegg and F. von Meissner (Monatsh., 1928, 50, 55—60).—All attempts to obtain a monosulphonyl chloride from phenol, anisole, phenetole, phenyl acetate, thioanisole, or acetylthiolbenzene by the action of chlorosulphonic acid were unsuccessful, disulphonyl chlorides being obtained. Anisole gives anisole-2 : 4-disulphonyl chloride, m. p. 86°, from which the 2 : 4-*disulphonamide*, m. p. 239—240°, and 2 : 4-*disulphanilide*, m. p. 209°, are obtained; the chloride is reduced with zinc and sulphuric acid to 2 : 4-*dithiolanisole*, m. p. 51°. Phenetole gives the 2 : 4-disulphonyl chloride, m. p. 102—104°, and thence the 2 : 4-*disulphanilide*, m. p. 202—204°, is obtained. *Acetoxybenzene*-2 : 4-*disulphonyl chloride*, m. p. 91°, is obtained by acetylation of phenol-2 : 4-disulphonyl chloride, which is the only product of the action of chlorosulphonic acid on phenyl acetate; 3-*acetoxytoluene*-4 : 6(?2)-*disulphonyl chloride*, m. p. 109°, is similarly prepared. Acetylthiolbenzene and chlorosulphonic acid give only 4 : 4′-di(chlorosulphonyl)diphenyl disulphide, m. p. 131°. C. Hollins.

Nitration of *m*-fluorophenol. H. H. Hodgson and J. Nixon (J.C.S., 1928, 1879—1882).—The methods of preparation of the undermentioned compounds are those described for the corresponding chloro- and bromo-compounds with appropriate modifications (cf. A., 1925, i, 1144; 1926, 281). The following are described: 3-*fluoro*-6-*nitrophenol*, m. p. 32° (*sodium* and *silver* salts; *methyl ether*, m. p. 52°; *benzoate*, m. p. 110—111°); 3-*fluoro*-4-*nitrophenol*, m. p. 42° (*sodium* and *silver* salts; *methyl ether*, m. p. 56·5°; *benzoate*, m. p. 118°); 3-*fluoro*-2-*nitrophenol*, m. p. 39° (*sodium* and *silver* salts; *methyl ether*, m. p. 43·5°; *benzoate*, m. p. 114°); 3-*fluoro*-4 : 6-*dinitrophenol*, m. p. 80° (*silver* salt); 3-*fluoro*-2 : 6-*dinitrophenol*, m. p. 68·5° (*silver* salt); 3-*fluoro*-2 : 4-*dinitrophenol*, m. p. 138—139° (*silver* salt); 3-*fluoro*-2 : 4 : 6-*trinitrophenol*, m. p. 173° (*silver* salt). The 3-fluoro-2-, -4-, and -6-nitrophenols resist acetylation. Monosulphonation of 3-fluoro-2-nitrophenol in the cold or at 100—120° appears to give exclusively 3-fluoro-2-nitrophenol-4-sulphonic acid, since only 3-fluoro-2 : 6-dinitrophenol could be obtained by further mononitration. The differences in behaviour of the fluoro- and the other halogeno-analogues, more especially of their silver salts, are discussed. A trustworthy method for the preparation of *m*-fluoronitrobenzene from *m*-nitroaniline is described. M. Clark.

Basicity of nitrophenoxymalonic acids. J. S. Teletov and N. N. Andronikov (J. Russ. Phys. Chem. Soc., 1927, 59, 1199—1204).—The conductivities of the sodium salts of bis-*o*-, -*p*-, and -*m*-nitrophenoxymalonic acids were investigated by the Ostwald–Walden method, to determine their basicity, $(V_{1024}-V_{32})/10$.

The ultra-violet absorption spectra of Bischoff's isomerides of the methyl and ethyl esters of bis-*p*-phenoxymalonic acids showed that these were mixed crystals of the malonic and corresponding disubstituted acetic esters formed by loss of a carboxyl group. The sodium salts of the *o*- and *m*-acids, prepared from their methyl esters, gave values 1·98—1·99 for the basicity. The sodium salt of the *p*-acid, prepared by five different methods, gave values for the basicity from 2·18 to 2·06, *i.e.*, the acid is somewhat stronger than the *o*- and *m*-isomerides. Investigation of the mono-substituted *p*-phenoxymalonic acid showed it to be a distinctly weaker dibasic acid than the disubstituted acids, the value obtained being 1·54. M. Zvegintzov.

Complex isomerism and complex salt isomerism. E. Hertel and J. van Cleef (Ber., 1928, 61, [*B*], 1545—1549).—The Debye–Scherrer diagrams of the yellow, m. p. 91·5°, and the red form, m. p. 84·5°, of the compound formed from 2 : 6-dinitrophenol and 4-bromo-α-naphthylamine are so different from one another that the existence of different crystal lattices is placed beyond doubt. The case is classified as complex isomerism.

2 : 4 : 6-Trinitroanisole and β-naphthyldimethylamine afford a *compound*, m. p. 68—69°, to which the constitution $OMe{\cdot}C_6H_2(NO_2)_3 \ldots C_{10}H_7{\cdot}NMe_2$ is ascribed. When heated above its m. p., it becomes converted into *trimethyl*-β-*naphthylammonium picrate*, m. p. 190° (decomp.), identical with the product derived from trimethyl-β-naphthylammonium iodide and silver picrate. The reverse transformation cannot be effected. To this relationship the term "complex salt isomerism" is applied. The types of isomerism are illustrated by the phase diagrams of the compounds. H. Wren.

Interaction of picric acid and 2 : 5-diketopiperazine. A. Morel and P. Preceptis (Compt. rend., 1928, 187, 236—239).—When boiled in aqueous solution picric acid and diketopiperazine give glycylglycine picrate, the reaction thus involving hydrolysis of a ·CO·NH· group in the diketopiperazine ring, followed by salt formation. The coloration afforded in presence of sodium carbonate (Sasaki, A., 1921, ii, 358) or barium hydroxide is due to the formation of azo-derivatives, in addition to the picrate of glycylglycine, a reaction comparable with that observed by Seyewetz and Mounier (this vol., 167), and also resembling the reduction caused by creatinine. The formation of azo-derivatives in these conditions is regarded as confirming the reasons already advanced by Abderhalden and Komm (A., 1924, i, 1361) for the existence in the proteins of rings containing equivalent carbonyl groups. R. Brightman.

[Nuclear condensation of phenols with nitriles.] J. Houben (Ber., 1928, 61, [*B*], 1597).—A reply to Hoesch (this vol., 169). H. Wren.

Reactions of Friedel and Crafts, Fries, and Gattermann. K. von Auwers and W. Mauss (Ber., 1928, 61, [*B*], 1495—1507).—The Friedel–Crafts reaction occurs in very differing ways with various polyalkylated phenolic ethers and the constitution of the products must be elucidated in each individual case. With phenols of certain structure, *meta*-derivatives may be the main products of the change. In the case of the Fries displacement this has never been observed. A difference appears therefore to be involved according as the acid residue is introduced from without into the molecule or is originally present therein. In contrast to the Friedel–Crafts change, the Fries displacement takes place within the molecule; the reactions are essentially different. There is little evidence of the formation of *meta*-derivatives in the Gattermann synthesis, but displacement of alkyl groups occurs as readily as during the Fries reaction.

as-*m*-Xylyl methyl ether is converted by acetyl chloride in the presence of carbon disulphide and aluminium chloride into a mixture of 5-acetyl-*as*-m-xylenol, m. p. 53—54°, and 6-*acetyl*-as-m-*xylenyl methyl ether*, b. p. 140—142°/13 mm., m. p. 50—51°. Hydrolysis of the latter compound with aluminium chloride affords 6-acetyl-*as*-*m*-xylenol, m. p. 130—131·5° (*oxime*, m. p. 142—146°, and its *hydrochloride*), converted by 80% phosphoric acid at 170—190° into *as*-*m*-xylenol. Similarly, chloroacetyl chloride affords 5-chloroacetyl-*as*-*m*-xylenol and 6-*chloroacetyl*-as-m-*xylenol*, m. p. 107—107·5°, reduced by zinc dust and acetic acid to 6-acetyl-*as*-*m*-xylenol. 4-*Methyl*-2-*ethylphenyl methyl ether*, b. p. 206—208°, is transformed by the Friedel–Crafts reaction into 5-*acetyl*-

4-*methyl-2-ethylphenyl methyl ether*, b. p. 148—150°/16 mm., 6-acetyl-4-methyl-2-ethylphenol, b. p. 144—146°/25 mm. (*p*-nitrophenylhydrazone, m. p. 175—176°), and 5-*acetyl-4-methyl-2-ethylphenol*, m. p. 120—121° (converted by phosphoric acid into 4-methyl-2-ethylphenol, identified as its phenylurethane, m. p. 100—101°). The *oxime* of the hydroxyphenol yields a *hydrochloride*. Reduction of the hydroxy-ketone by Clemmensen's method affords 4-*methyl*-2 : 5-*diethylphenol*, b. p. 248—250°, m. p. 54—54·5° (*methyl ether*, b. p. 234—236°). Mesityl methyl ether reacts with difficulty with aluminium chloride in presence of carbon disulphide, forming m-*acetylmesitol*, m. p. 81—82°.

as-m-Xylenyl benzoate is converted by aluminium chloride at 130—140° into 5-*benzoyl*-as-m-*xylenol*, m. p. 40—41° (*oxime*, m. p. 153—154°), and 6-*benzoyl*-as-m-*xylenol*, m. p. 140—141°. *p*-Xylenyl acetate and aluminium chloride at 80—90° afford 6-acetyl-*p*-xylenol, m. p. 130—131°, and 5-acetyl-*as-m*-xylenol, m. p. 54°. 2 : 5-*Dimethyl*-4-*ethylphenol*, m. p. 39—40°, is converted into its *acetate*, b. p. 248—250°, which, with aluminium chloride at 250°, yields 6-acetyl-2 : 4-dimethyl-3-ethylphenol. 2 : 5-*Diethyl*-4-*methylphenyl acetate*, b. p. 260—262°, and aluminium chloride at 130° give 6-acetyl-4-methyl-2 : 3-diethylphenol amongst other products.

Mesityl methyl ether is not readily brought into reaction with hydrocyanic acid in Gattermann's synthesis, but appears to yield small amounts of 3-hydroxy-2 : 4 : 6-trimethylbenzaldehyde, m. p. 108—109°, reduced by Clemmensen's method to (?) 2 : 3 : 4 : 6-tetramethylphenol. Under somewhat different conditions a *hydroxydimethylbenzaldehyde*, m. p. 106—107° (*oxime*, m. p. 164·5—165°), is obtained. *vic-o*-Xylenol gives mainly 4-hydroxy-2 : 3-dimethylbenzaldehyde; an *o*-hydroxyaldehyde is produced in small amount. *vic*-Hemellithenol yields *p*-hydroxydimethylbenzaldehyde and 2-*hydroxy*-3 : 4 : 5-*trimethylbenzaldehyde*, m. p. 36—37°.

H. Wren.

Flueckiger's test for thymol and carvacrol. H. G. Hewitt (J. Amer. Pharm. Assoc., 1928, 17, 524—525).—The test consists in warming the substance in chloroform solution with solid sodium hydroxide. Thymol or carvacrol gives a red coloration, due to the formation of an aldehyde and the condensation of the latter with the phenol (Flueckiger, Pharm. Chem., 1888, 2, 101). E. W. Wignall.

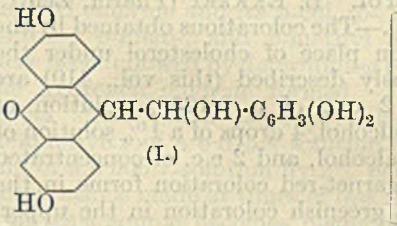
[Oil from] corolla of *Monarda fistulosa*, L. K. H. Rang (J. Amer. Pharm. Assoc., 1928, 17, 525—528).—The volatile oil from the florets of this species has $d^{23.3}$ 0·9740 and contains carvacrol and some hydroxythymoquinone; the alcoholic extract contains two *substances*, m. p. 139—141° and 235—237°.

E. W. Wignall.

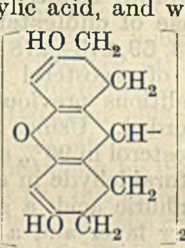
Sclareol, the chief constituent of oil of sage. Y. Volmar and A. Jermstad (J. Pharm. Chim., 1928, [viii], 8, 55—57).—See this vol., 524.

Oxidation of sulphides with perbenzoic acid. II. Preparation of sulphoxides and sulphones and a titrimetric method for determination of sulphoxides. L. N. Lewin (J. pr. Chem., 1928, [ii], **119**, 211—217).—ββ'-Dichlorodiethyl sulphide, diphenyl sulphide, and dibenzyl sulphide are oxidised quantitatively to sulphoxides provided that the theoretical quantity of perbenzoic acid is used in dilute, well-cooled chloroform solution. The sulphoxides are converted by 15% excess of perbenzoic acid into sulphones, the yields being 100%, 100%, and 80%, respectively. C. Hollins.

Action of oxalyl chloride on resorcinol. J. Mikšić (J. pr. Chem., 1928, [ii], **119**, 218—230).—By the action of sodium and excess of oxalyl chloride on resorcinol in moist ether, first with cooling and finally at the boil for a few days, there is obtained "β-*resemin*," $C_{20}H_{16}O_6$ (I), m. p. 155—160° (decomp.) (*penta-acetyl* derivative, m. p. 197°), which by fusion with alkali at 200° gives β-resorcylic acid, and when distilled with zinc dust xanthen and resorcinol. From oxalyl chloride (1 mol.), resorcinol (2 mols.), and potassium (2 atoms) in moist ether there are obtained "*resjankin*," $C_{26}H_{26}O_6$ (II), decomp. 280° (*tetra-acetyl* derivative, m. p. 170—172°, and "*resperin*," $C_{20}H_{16}O_7$ (III), m. p. 210° (decomp.; *hexa-acetyl* derivative, m. p. 159—159·5°). The absorption spectra of the three compounds are compared with those of phenolphthalein and fluorescein.



(I.)



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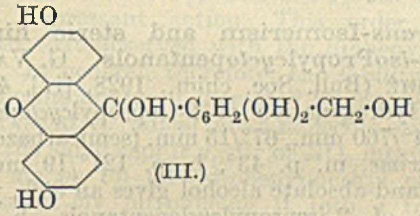


(III.)

C. Hollins.

Aromatic allyl and propenyl compounds. I. Safrole and *iso*safrole. H. I. Waterman and R. Priester (Rec. trav. chim., 1928, 47, 849—860).—Safrole, purified through its mercuriacetate (Manchot, A., 1920, i, 780), has m. p. and setting point 11·0°, b. p. 38—40° in a cathode-vacuum, or 125—126°/25 mm., d_4^{20} 1·100, n_D^{20} 1·5383. *iso*Safrole, purified through the picrate, shows b. p. 46·8° in a cathode-vacuum, d_4^{20} 1·122, n_D^{20} 1·5782. The pure compounds do not react with iodine in the dark, and unsaturated impurities may thus be detected. In the light safrole takes up more iodine than *iso*safrole and reaches equilibrium more quickly. A method for analysing mixtures of the two isomerides based on their different affinities for iodine is described. C. Hollins.

Action of ethylamine and diethylamine on *iso*safrole oxide. J. S. Kusner (J. Russ. Phys. Chem. Soc., 1928, 60, 655—659).—The formation by the action of ethylamines on *iso*safrole oxide of amino-alcohols was studied, with the view of investigating their possible physiological properties. *iso*-Safrole oxide, b. p. 147—149°/15 mm. (prepared by the action of alcoholic potassium hydroxide on the bromohydrin), gave with ethylamine on keeping for 3 days at 30—40° in a solution of aqueous alcohol, a white *compound*, m. p. 67°, b. p. 175—180°/15 mm., with the properties of a secondary alcohol and a base, probably having the constitution $CH_2O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CHMe{\cdot}NHEt$ (*hydrochloride*, m. p. 181°; *picrate*, m. p. 168—169°). With ethylamine, the reaction was more difficult, requiring heating for 4 hrs. at 100°. A very viscous *liquid*, b. p. 174—178°/15 mm., soluble in ether, acetone, and alcohol was obtained, giving a *picrate*, m. p. 160°, and *hydrochloride*, m. p. 196—197°.

M. Zvegintzov.

Colour reactions of ergosterol as distinct from those of cholesterol. L. Ekkert (Pharm. Zentr., 1928, 69, 276—278).—The colorations obtained by the use of ergosterol in place of cholesterol under the conditions previously described (this vol., 410) are recorded. Using 2 c.c. of a 0·125% solution of ergosterol in 96% alcohol, 4 drops of a 1% solution of furfuraldehyde in alcohol, and 2 c.c. of concentrated sulphuric acid, a garnet-red coloration forms in the lower layer and a greenish coloration in the upper. Treatment of 2 c.c. of a dilute acetic anhydride solution of the sterol with 2 c.c. of 85% phosphoric acid gives a greenish-yellow coloration after long keeping in the case of cholesterol and a brilliant green coloration in the case of ergosterol.

G. A. C. Gough.

cis–trans-Isomerism and steric hindrance. VII. 2-_iso_Propyl_cyclo_pentanols. G. Vavon and A. Apchié (Bull. Soc. chim., 1928, [iv], 43, 667—677).—Hydrogenation of 2-*iso*propyl*cyclo*pentanone, b. p. 174°/760 mm., 67°/15 mm. (semicarbazone, m. p. 202°; *oxime*, m. p. 43°, b. p. 121°/19 mm.), with sodium and absolute alcohol gives an 85% yield of a mixture of 2-*iso*propyl*cyclo*pentanols, b. p. 85°/18 mm., in which the *trans*-isomeride predominates. trans-2-iso*Propyl*cyclo*pentanol*, isolated by means of the *hydrogen phthalate*, m. p. 69°, has b. p. 93—94°/27 mm., d_4^{11} 0·910, n_D^{11} 1·4583; the trans-*hydrogen succinate*, d_4^{11} 1·073, n_D^{11} 1·463, and *phenylurethane*, m. p. 63°, are described. Hydrogenation in presence of platinum-black in acetic acid containing 10% of aqueous hydrochloric acid affords a mixture of 2-*iso*propyl*cyclo*pentanols (together with some acetate) in which the cis-*isomeride*, b. p. 84—85°/20 mm., d_4^{11} 0·9145, n_D^{11} 1·4578 (*hydrogen phthalate*, m. p. 105°; *phenylurethane*, m. p. 103°; *hydrogen succinate*, m. p. 48—49°), preponderates, but not to the extent obtaining with the 2-*iso*propyl*cyclo*hexanols (A., 1927, 455). When heated in nitrogen at 180—190° for 6 hrs. the sodium derivative of the *cis*- is largely converted into the *trans*-isomeride. With acetic acid at 0° in presence of 2% of sulphuric acid the *trans*- is esterified about three times as rapidly as the *cis*-isomeride; at 39° or in the absence of a catalyst the difference is less marked. Similarly, the *trans*-hydrogen phthalate and -hydrogen succinate are hydrolysed more rapidly than the corresponding *cis*-compounds, the ratio of the velocity coefficients varying from 4·5 to 5 for the hydrogen phthalates in 75% alcohol at 39° and 68°, and from 9 to 16 in water at 68° and 0°. For the hydrogen succinate the corresponding ratios at 0° and 39° are 18 and 10 in 75% alcohol, respectively, and 19 and 15 in water. Since these ratios are smaller than those observed (*loc. cit.*) for the corresponding 2-*iso*propyl*cyclo*hexanols although the velocity coefficients themselves are larger, it is concluded that the steric effect of the *iso*propyl group is less marked in the *cyclo*pentanols than in the *cyclo*hexanols, a view which is supported by the lesser formation of the *cis*-*iso*propyl*cyclo*pentanol in catalytic hydrogenation.

*cyclo*Pentanone, b. p. 129°, is obtained in 87% yield by treatment of adipic acid for 16 hrs. with 1·5% of barium hydroxide; larger amounts of barium lower the yield. Condensation of *cyclo*pentanone with excess of acetone at −10° in presence of dilute sodium methoxide gives a 39% yield of 2-*iso*propylidene*cyclo*pentanone, b. p. 78—79°/10 mm. (*oxime*, m. p. 83°), together with 2-*cyclo*pentylidene*cyclo*pentanone, b. p. 115—118°/10 mm. (oxime, m. p. 122°), di-iso*propylidene*cyclo*pentanone*, m. p. 41°, b. p. 130—140°/11 mm., and iso*propylidene*cyclo*pentylidene*cyclo*pentanone*, m. p. 37°, b. p. 167—175°/11 mm.

R. Brightman.

Relative stability of isomerides and absorption spectra. Transformations in the glycol and aldehyde series. (Mme.) Ramart-Lucas and F. Salmon-Legagneur (Compt. rend., 1928, 186, 1848—1850; cf. this vol., 760).—Rules given for the prediction of intramolecular transformations from absorption spectra (*loc. cit.*) have been followed to obtain aldehydes or ketones by the dehydration of glycols by heat, and also to transform an aldehyde into a ketone. From these rules dehydration of glycols at one temperature should yield aldehydes and at a higher temperature ketones. The dehydration of αα-diphenylethyleneglycol, β-phenylbutane-αβ-diol, and hydrobenzoin was effected by passing their vapours through a tube containing infusorial earth, at reduced pressure, whereby secondary reactions were avoided. At 250—300° primary–tertiary glycols yielded only aldehydes and at 400—450° only ketones. At 250—300° hydrobenzoin yielded diphenylacetaldehyde, a little deoxybenzoin, and unchanged glycol, whilst at 400—450° phenyl benzyl ketone and a little benzaldehyde (from the dissociation of hydrobenzoin) were obtained. It is suggested that an aldehyde is first formed on dehydration and equilibrium between aldehyde and ketone is set up, with displacement in the direction of ketone at higher temperatures, the latter substance having absorption bands nearer the visible region. Thus diphenylacetaldehyde when treated in the same manner as the glycols was converted into deoxybenzoin at 400—450°, which result supports the theory. An ethylene oxide is suggested as intermediate in the change from glycol to aldehyde.

J. D. Fulton.

Reactivity of atoms and groups in organic compounds; the carbon–chlorine bond. J. F. Norris. **III.** [with A. A. Morton]. **Rate of reaction between diphenylmethyl chloride and ethyl alcohol. IV** [with C. Bantal]; **V** [with J. T. Blake]. **Rates of reaction between derivatives of diphenylmethyl chloride and ethyl or _iso_propyl alcohol. VI** [with D. V. Gregory]. **Rates of reaction of benzoyl chloride and some derivatives**

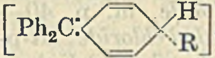
with *iso*propyl alcohol (J. Amer. Chem. Soc., 1928, 50, 1795—1803, 1804—1808, 1808—1812, 1813—1816). III.—In order to examine the effect of substituents on the strength of the carbon–chlorine linking, the rates of formation of hydrogen chloride from a large number of alkyl or acyl chlorides and ethyl or *iso*propyl alcohol have been conductometrically determined. Goldschmidt's values for the conductivity of absolute ethyl-alcoholic hydrogen chloride (A., 1915, ii, 136) have been confirmed by further measurements. An approximate correction for the effect of non-electrolytes on the conductivity of alcoholic hydrogen chloride has been obtained by correlating the percentage lowering of the specific conductivity produced by 8 hydrocarbons and halogenobenzenes with their mol. volumes. The velocity of reaction of diphenylmethyl chloride with ethyl alcohol in 0·1—0·02*N* solution at 25° corresponds closely with that required for a reversible unimolecular reaction. The velocity coefficient in the forward direction (k_1), calculated by a new method, is not affected by as much as 10% of impurity in the diphenylmethyl chloride, but is increased by traces of water. On this account, higher values are obtained for k_1 by titration measurements. Experiments at 0° give a value of about 4 for the temperature coefficient, k_{t+10}/k_t, of the forward reaction.

IV. The values of k_1, calculated by the above method, are tabulated for 15 mono- and di-substituted diphenylmethyl chlorides and ethyl alcohol at 25°, diphenylmethyl chloride itself being unity. The positive effect of substituents on the mobility of the chlorine atom is greatest in the *p*-position and is not parallel with the orienting effect in aromatic substitution. The order of influence of *p*-substituents is $OMe > OPh > Et > Me > Ph > C_{10}H_7 > Cl > Br$, the last two having a depressant effect which is greatest in the *o*-position. This is in good agreement with the order found by Olivier (A., 1923, i, 197, 908) for the hydrolysis of substituted benzyl chlorides. The methoxy- and phenoxy-diphenylmethyl chlorides are coloured and react much more readily with water and alcohols than does benzoyl chloride. There is no relation between the activating effect of a radical and its effect on the dissociation constant of an acid. Thus, *p*-toluic acid and phenylacetic acid are nearly equal in strength, but the values of k_1 for phenyl-*p*-tolylmethyl chloride and αβ-diphenylethyl chloride with ethyl alcohol are 16·2 and 0·0004, respectively. The velocity coefficients of the *pp*′-dichloro- and *pp*′-dimethyl-diphenylmethyl chlorides are approximately the squares of those for the corresponding monosubstituted derivatives. The mobility of the hydroxylic hydrogen in *iso*propyl alcohol calculated from k_1 for the reactions between this alcohol and diphenylmethyl chloride and its *pp*′-dichloro-derivative is 11% and 15%, respectively, of that of the hydroxylic hydrogen in ethyl alcohol (cf. A., 1925, i, 626). The following derivatives of diphenylmethyl chloride have been prepared from the corresponding carbinols by Montagne's method (A., 1907, i, 141): p-*phenyl*-, m. p. 71—72·5°; p-*chloro*-, b. p. 172—173°/6 mm.; p-*methyl*-, b. p. 147—148°/2 mm.; oily o-*chloro*-, decomp. 90°; pp′-*dimethyl*-, m. p. 41—43·5°, and p-*bromo*-, b. p. 188—191°/10 mm.

V. The following are described: *phenyl*-o-*tolylmethyl chloride*, m. p. 40—40·5°, red, oily *phenyl*-p-*anisylmethyl chloride*; *di*-p-*tolylmethyl chloride*, m. p. 45—46°; p-*phenoxydiphenylcarbinol*, m. p. 75°; orange p-*phenoxydiphenylmethyl chloride*, m. p. 49—50°; p-*ethyldiphenylcarbinol*, m. p. 33°; p-*ethyldiphenylmethyl chloride*, b. p. 122°/1—2 mm.; pink, oily *phenyl*-o-*anisylmethyl chloride*, *phenyl*-α-*naphthylmethyl chloride*, m. p. 64—64·5°; p-*bromodiphenylcarbinol*, m. p. 63°; oily *phenyl*-m-*tolylmethyl chloride*, and m-*chlorodiphenylmethyl chloride*. The reaction velocities of these chlorides with ethyl alcohol are tabulated and the results are discussed in the preceding section.

VI. The reactions between *iso*propyl alcohol and benzoyl chloride and its *p*-chloro-, *p*-bromo-, *p*-iodo-, *o*-nitro-, *p*-nitro-, and *p*-methyl derivatives at 25° have been followed by determining conductometrically the hydrogen chloride formed. Hydrogen chloride reacts slowly with *iso*propyl alcohol at 25°, the conductivity of a 0·075*N*-solution changing by 0·4% and of a 0·006*N*-solution by 2% per hr., but by using observations made at times of less than 1 hr. the error from this source becomes negligible for the present purpose. A correction is also introduced for the effect of the non-electrolytes. The reactions are unimolecular up to 30% conversion. The effect of *p*-substituents in increasing the mobility of the chlorine atom is in the order $NO_2 > Br > Cl > I > Me$, the last having a depressant action. This order is the opposite to that observed with the diphenylmethyl chlorides. In general, therefore, the lability of the carbon–chlorine linking is increased by introducing a positive or negative radical into a molecule containing groups of the same sign (*e.g.*, Br or NO_2 into benzoyl chloride; Me or Ph into diphenylmethyl chloride) and decreased by introducing it into a molecule containing groups of opposite sign.

H. E. F. Notton.

Colour, mol. wt., and electrolyte character of derivatives of triphenylmethane. I. Lifschitz and G. Girbes (Ber., 1928, 61, [*B*], 1463—1491).—Triphenylmethane derivatives can be divided into two classes of compounds, Ar_3CX. In the first series, the C–X linking is homopolar as far as can be ascertained. The substances are non-electrolytes and do not yield triphenylmethyl ions. Triphenylmethane, triphenylethane, their cyanides, azides, and sulphonic acids, belong to this series. In the second class, the C–X linking is heteropolar and can give rise to ions. This occurs only by intrusion of solvent or other molecules $[Ar_3CX]+R \rightleftharpoons [Ar_3C\cdots R]^{\cdot}+X'$. The incidence and extent of such intrusion depend on the nature of R and the tenacity of the group X in the first sphere. The electrolytes II are naturally not optically identical with the initial substances I, but the difference can usually be appreciated only in the ultra-violet. According to the nature of R, the electrolytes II may be colourless or coloured. Greatly deformable molecules R may cause absorption in the region of greater wave-length. Thus the thiocyanates are colourless when dissolved in alcohol or acetone, but yield more or less intense yellow or orange solutions in phenol. More pronounced colour may further be occasioned by structural modification of the cation, *e.g.*, by transformation to the quinonoid form, thus yielding compounds,  Diarylquinols show selective absorption in the visible part of the spectrum which does not, however, resemble that of dyes. Finally, an intruded molecule R (from a second molecule of the solvent) can function, thus giving *meri*quinonoid ions with pronounced dye-like absorption. Such autocomplex formation is particularly marked when the concentration is great, X has a pronounced tendency to ionisation, and the medium has slight intrusive power.

The derivatives of triarylmethylcarbinols exist in a colourless and a coloured series. Apart from the actual dye salts, the colour of the solutions depends on the concentration, temperature, and medium, the sequence of the latter being: ether, alcohol, acetone, nitrobenzene, acetonitrile, camphor, chloroform. Other things being equal, the colour increases with the concentration and, particularly, with the temperature. Among the actual dye salts of the rosaniline and malachite-green series, the transition colourless $\rightleftharpoons$ coloured by change of medium and temperature has not previously been observed. In addition to the coloured forms, however, colourless varieties are observed with the azides, ferrocyanides, and thiocyanates of malachite-green and crystal-violet which are particularly stable in the diamino-series in the increasing sequence, thiocyanate ⟶ ferrocyanide ⟶ azide. The photochemical transition, colourless $\rightleftharpoons$ coloured, cannot be studied with the azides which undergo decomposition under the influence of ultra-violet light. Solutions of malachite-green azide contain an equilibrium mixture of true dye salt and of a colourless form; this equilibrium is established with remarkable rapidity. If to such an almost colourless solution mercuric cyanide or thiocyanate is added, an intense colour is immediately developed owing to the formation of double salts with the dye salt. Similar equilibria exist in the cases of the salts of malachite-green etc. with mineral acids as evidenced by the production of the more intensely coloured complex compounds containing heavy metals, but in these cases the balance is displaced greatly towards the dye salt side. Only the typical, true methane compounds, particularly the cyanides, maintain an individual position. With these, transformation can be effected only by illumination. Precisely similar relationships are observed among the cyanides and azides of triphenylcarbinol and its methoxy-derivatives.

The cyanides of triphenyl-, diphenylanisyl-, phenyldianisyl-, and trianisyl-carbinols give colourless solutions with normal mol. wt. in all media. In the almost non-dissociating chloroform, the thiocyanates are unimolecular, although the solutions are slightly coloured; the values are independent of the concentration within experimental limits. In alcohol, the thiocyanates give values corresponding with 60—75% of the theoretical; the dissociation increases with increasing dilution and since the substances are completely stable in boiling alcohol, the phenomenon must be regarded as electrolytic dissociation. In confirmation, the solutions in contrast with those of the cyanides exhibit marked electrolytic conductivity. The compounds are therefore sharply differentiated from the typical, coloured carbonium salts of which the stable perchlorates of methoxylated triphenylcarbinols have been investigated. Their solutions in chloroform exhibit greatly exalted mol. wts. which increase markedly with increasing concentration. The relative intensity of colour increases in a similar manner. Identical relationships are found cryoscopically in camphor. In less intensely coloured solution in acetone, the mol. wt. is much lower and almost completely independent of the concentration. In freezing nitrobenzene (orange solution) trianisylcarbonium perchlorate exhibits low mol. wt. (the solution is a good conductor of electricity); in the boiling solvent (almost blackish-red solution) the results are much higher. The strongly coloured solutions of the perchlorates therefore invariably contain associated polymeric salt, the mol. wt. approaching the normal more closely as the solutions become less absorptive.

Under all conditions the cyanides and azides of triphenylcarbinol and methoxytriphenylcarbinols are non-electrolytes. This is also true of the cyanides of diamino- and triamino-triphenylmethane dyes. Preservation of the solutions, addition of complex-forming salts, and protracted heating do not induce electrolytic conductivity, which can be caused only by irradiation. In alcoholic solution malachite-green azide exhibits distinct electrolytic conductivity, which is less pronounced in its less intensely coloured solution in nitrobenzene. Colour and conductivity appear parallel. In harmony, both are increased by the addition of anionic-complex-forming substances, such as mercuric cyanide. Comparison of the behaviour of solutions of malachite-green chloride with those of normal electrolytes shows that the former must contain a proportion of undissociated colourless form. In these cases, the position of the equilibrium depends on the medium; the relative conductivity diminishes in the sequence alcohol, acetone, acetonitrile, nitrobenzene. This is most clearly shown with the ferrocyanides of triphenyl- and the methoxytriphenyl-carbinols. These colourless salts afford colourless or very feebly coloured triarylmethyl ions and thus are completely analogous to the corresponding thiocyanates. Solutions of the latter do not immediately attain their maximum conductivity unless heated. The perchlorates, as typical carbonium salts, have been investigated in the same media. In alcohol, the slight difference in conductivity between the yellow trianisylcarbonium salts and the colourless mono- and di-anisyl compounds is remarkable. The relatively high values of μ, in comparison with tetraethylammonium salts, is probably not due to alcoholysis. In acetone, the colour disappears or diminishes abnormally with dilution, whereas conductivity increases normally. This is possible only if the triarylmethyl ion, $[Ar_3C\cdots COMe_2]$, is colourless or only faintly coloured and the intensely coloured ions produced at a higher temperature are more highly complex or *meri*quinonoid. Similar observations are made in acetonitrile. In nitrobenzene, between 5° and 150°, the temperature coefficients of carbonium and ammonium salts diminish continuously with rise of temperature, whereas the colour of the carbonium solutions deepens from orange to dark red. Colour therefore has no influence on conductivity but is intimately associated with increase of mol. wt.

The following new compounds or amended data are recorded: tri-*p*-anisylmethane, m. p. 49°, which gives a red colour with sulphuric acid; tri-*p*-anisylcarbinol, m. p. 82°; phenyldi-*p*-anisylmethane, m. p. 99—100°; phenyldi-*p*-anisylcarbinol; *tri*-p-*anisylmethyl perchlorate*, m. p. 193°; phenyldi-*p*-anisylmethyl perchlorate, m. p. 210° (instead of m. p. 113—114°, as recorded); *diphenyl*-p-*anisylmethyl perchlorate*, m. p. 191°; triphenylmethyl perchlorate, m. p. 150°; tri-*p*-anisylacetonitrile, m. p. 128°; *phenyldi*-p-*anisylacetonitrile*, m. p. 95°; *diphenyl*-p-*anisylacetonitrile*, m. p. 117—118°; from the chloride and mercuric cyanide; *tri*-p-*anisylmethyl thiocyanate*; *phenyldi*-p-*anisylmethyl thiocyanate*, m. p. 112°, from the corresponding perchlorate in chloroform and potassium thiocyanate; *diphenyl*-p-*anisylmethyl thiocyanate*, m. p. 72°; *triphenylmethyl azide*, m. p. 65°, from the perchlorate in chloroform and sodium azide; *tri*-p-*anisylmethyl azide*, m. p. 74°; *malachite-green azide*, m. p. 118—119°; *tri*-p-*anisylmethyl ferrocyanide*, m. p. 230° (decomp.); *phenyldi*-p-*anisylmethyl ferrocyanide*, m. p. 192° (also $+CHCl_3$); *diphenyl*-p-*anisylmethyl ferrocyanide*, m. p. 238° (decomp.) (also $+ CHCl_3$); *triphenylmethyl ferrocyanide*, m. p. 280° after darkening at 270° (also $+2CHCl_3$); *p*-dimethylaminobenzylideneacetone, tile-red crystals, m. p. 128°, or yellow leaflets, m. p. 135°. H. WREN.

Preparation of phenolsulphonephthalein and bromo[phenol]sulphonephthalein. R. FREAS and E. A. PROVINE (J. Amer. Chem. Soc., 1928, **50**, 2014—2017).—Phenolsulphonephthalein is conveniently prepared by heating together saccharin (1 mol.), phenol (5 mols.), and sulphuric acid (4 mols.) at 120° for at least 48 hrs. More colouring matter is produced at higher temperatures, but it contains sulphonic acids. Addition of metallic sulphates affects the yield unfavourably. Aluminium, zinc, and ferric chlorides, and phosphoric acid (85%) are inferior to sulphuric acid as condensing agents. The dye is purified by repeated precipitation from sodium carbonate solution, and is then suitable for conversion into pure bromophenol-blue (tetrabromophenolsulphonephthalein).
H. E. F. NOTTON.

Benzyl chloromethyl ether and dibenzylformal. P. CARRÉ (Bull. Soc. chim., 1928, [iv], **43**, 767—768).—See this vol., 880.

***cyclo*Propylmethyl-alkylacetic acids, and their bactericidal action towards *B. lepræ*. XIII.** J. A. ARVIN and R. ADAMS (J. Amer. Chem. Soc., 1928, **50**, 1983—1985).—Toxicity towards *B. lepræ* is not evident in members below *cyclo*propylmethyloctylacetic acid and reaches a maximum in the acids containing 16 or 17 carbon atoms. The bactericidal effect does not differ markedly from that of acids of the same mol. wt. containing 5- or 6-membered rings. *cyclo*Propylmethyl bromide (cf. von Braun, A., 1925, i, 1401), the preparation of which is detailed, is converted by standard methods into *ethyl* cyclo*propylmethylmalonate*, b. p. 129—133°/18 mm., n_D^{20} 1·4363, d_4^{20} 1·0216, and the following *ethyl* cyclo*propylmethyl*-n-*alkyl-malonates* (the b. p. n_D^{20}, and d_4^{20} of each being given): *-amyl-*, 122—125°/1·7 mm., 1·4459, 0·9770; *-hexyl-*, 139—142°/2·9 mm., 1·4470, 0·9685; *-heptyl-*, 146—149°/2·7 mm., 1·4481, 0·9613; *-octyl-*, 149—154°/2·3 mm., 1·4491, 0·9559; *-nonyl-*, 165—168°/2·5 mm., 1·4503, 0·9512; *-decyl-*, 162—166°/1·9 mm., 1·4510, 0·9460; *-undecyl-*, 186—189°/3 mm., 1·4519, 0·9419; *-dodecyl-*, 183—187°/2 mm., 1·4526, 0·9395; *-tetradecyl-*, 192—195°/1·9 mm., 1·4530, 0·9377; and cyclo*propylmethyl*-n-*alkyl-acetic acids*: *-amyl*, 112—115°/1·4 mm., 1·4469, 0·9375; *-hexyl-*, 130—132°/1·8 mm., 1·4498, 0·9253; *-heptyl-*, 136—139°/2 mm., 1·4509, 0·9236; *-octyl-*, 146—149°/2·1 mm., 1·4529, 0·9142; *-nonyl-*, 162—164°/2·3 mm., 1·4545, 0·9105; *-decyl-*, 176—178°/2·7 mm., 1·4553, 0·9064; *-undecyl-*, m. p. 27—28°, b. p. 186—189°/3 mm.; *-dodecyl-*, m. p. 29—30°, b. p. 191—195°/3 mm.; and *-tetradecyl-*, m. p. 35—37°, b. p. 176—179°/1·3 mm. H. E. F. NOTTON.

β-Δ^2-*cyclo*Pentenylethyl-alkylacetic acids and their bactericidal action towards *B. lepræ*. XII. J. A. ARVIN and R. ADAMS (J. Amer. Chem. Soc., 1928, **50**, 1790—1794; cf. this vol., 754).—As in other series, the toxicity of these acids, and of some new *cyclo*pentenyl-alkylacetic acids, reaches a maximum with the members containing 16—18 carbon atoms. In all series hitherto examined, acids of approximately the same mol. wt., whether saturated or unsaturated, are nearly equal in bactericidal power. β-Δ^2-*cyclo*Pentenylethyl alcohol (cf. Noller and Adams, A., 1926, 1137) is converted by standard methods into β-Δ^2-cyclo*pentenylethyl bromide*, b. p. 71—72°/16 mm., n_D^{20} 1·4995, d_4^{20} 1·2869; δ-Δ^2-cyclo*pentenylbutyl alcohol*, b. p. 118—123°/24 mm., n_D^{20} 1·4723, d_4^{20} 0·9317 (*by-product*, b. p. 98—103°/24 mm.); δ-Δ^2-cyclo*pentenylbutyl bromide*, b. p. 82—86°/5 mm., n_D^{20} 1·4942, d_4^{20} 1·2229; *ethyl* δ-Δ^2-cyclo*pentenylbutylmalonate*, b. p. 152—155/3 mm., n_D^{20} 1·4598, d_4^{20} 1·0077, and δ-Δ^2-cyclo*pentenylbutylacetic acid*, b. p. 149—154°/5 mm., n_D^{20} 1·4740, d_4^{20} 0·8962. The b. p., n_D^{20} and d_4^{20}, respectively, of the following are: *ethyl* β-Δ^2-cyclo*pentenylethyl-alkyl-malonates*: -n-*hexyl-*, 152—155°/2 mm., 1·4598, 0·9742; -n-*heptyl-*, 159—162°/1·4 mm., 1·4602, 0·9649; -n-*octyl-*, 178—181°/2 mm., 1·4605, 0·9624; -n-*nonyl-*, 176—180°/1·5 mm., 1·4609, 0·9567; -n-*decyl-*, 183—187°/2·1 mm., 1·4613, 0·9531; -n-*undecyl-*, 190—194°/2·1 mm., 1·4616, 0·9486, and -n-*dodecyl-*, 197—201°/2·2 mm., 1·4618, 0·9460; *ethyl* Δ^2-cyclo*pentenyl-alkyl-malonates*: -n-*decyl-*, 170—172°/1·5 mm., 1·4616, 0·9642; -n-*undecyl-*, 176—180°/1 mm., 1·4622, 0·9598, and -n-*dodecyl-*, 193—196°/2 mm., 1·4627, 0·9559; β-Δ^2-cyclo*pentenylethyl-alkyl-acetic acids*: -n-*hexyl-*, 160—163°/2·3 mm., 1·4697, 0·9426; -n-*heptyl-*, 166—168°/2·2 mm., 1·4698, 0·9358; -n-*octyl-*, 174—176°/1·8 mm., 1·4700, 0·9315; -n-*nonyl-*, 183—185°/2 mm., 1·4701, 0·9269; -n-*decyl-*, 186—188°/1·5 mm., 1·4702, 0·9227; -n-*undecyl-*, 190—193°/1·3 mm., 1·4703, 0·9196, and -n-*dodecyl*, 199—203°/1·5 mm. (m. p. 30—31·5°); Δ^2-cyclo*pentenyl-alkyl-acetic acids*: -n-*decyl-*, 183—186°/1·5 mm., 1·4692, 0·9319; -n-*undecyl-*, 188—190°/1·5 mm. (m. p. 36—38°); -n-*dodecyl-*, 202—204°/2 mm. (m. p. 38—39°); and β-Δ^2-cyclo*pentenylethylacetic acid*, 125—126°/4 mm., 1·4718, 0·9904. [With C. R. NOLLER]. Magnesium β-Δ^2-*cyclo*pentenylethyl bromide and methyl η-aldehydo-octoate yield θ-*hydroxy*-κ-Δ^2-cyclo*pentenyl*-

undecoate, b. p. 177—179°/2 mm., n_D^{20} 1·4720, d_4^{20} 0·9874, which is hydrolysed by alcoholic potassium hydroxide to θ-*hydroxy*-κ-Δ^2-cyclo*pentenylundecoic acid* (θ-*hydroxy*-dl-*hydnocarpic acid*), m. p. 62·0—62·8°. H. E. F. Notton.

Thermal decomposition of thiobenzanilide. A. W. Chapman (J.C.S., 1928, 1894—1897).—Thiobenzanilide decomposes when heated at 250° or higher temperatures yielding hydrogen sulphide (37—40%), 1-phenylbenzthiazole (I), (38—58%), *s*-diphenylbenzamidine (II) (11—19%), stilbene, and tetraphenylthiophen (III) (cf. Jacobson, A., 1886, 700). The following mechanism is suggested : $Ph\cdot CS\cdot NHPh \longrightarrow PhC{<}\genfrac{}{}{0pt}{}{N}{S}{>}C_6H_4$ (I) $+2H$. $2H+Ph\cdot CS\cdot NHPh \longrightarrow NH_2Ph+Ph\cdot CHS$. $NH_2\cdot Ph+Ph\cdot CS\cdot NHPh \longrightarrow NPh{:}CPh\cdot NHPh$ (II) $+H_2S$. $Ph\cdot CHS \xrightarrow{\text{heat}} CHPh{:}CHPh+\genfrac{}{}{0pt}{}{CPh{:}CPh}{CPh{:}CPh}{>}S$ (III) $+H_2S$ (cf. Baumann and Klett, A., 1892, 185). M. Clark.

Bromination of *p*-aminobenzoic acid and its ethyl and butyl esters. A. Leulier and J. Dinet (J. Pharm. Chim., 1928, 8, [viii], 57—61; cf. A., 1927, 1186).—According to the concentration of hydrobromic acid employed, *monobromo*-, m. p. 225° (Maquenne block), and dibromo- (chars 320°) derivatives of *p*-aminobenzoic acid have been obtained in yields of 60% and 57%, respectively, by the action of hydrogen peroxide on a solution of the amino-acid in aqueous hydrobromic acid. Bromination of the ethyl ester gave 80% of the monobromo-compound, m. p. 92°, and the butyl ester gave 90% of monobromo-derivative, m. p. 63°. The esters did not appear to have lost their anæsthetic properties nor did the toxicity appear to be increased by bromination. Under similar conditions, the nitrobenzoic acids are not brominated. E. H. Sharples.

Action of organo-magnesium compounds on *N*-substituted cinnamic anilides. N. Maxim and N. Ioanid (Bul. Soc. Chim. România, 1928, 10, 29—48; cf. Maxim, this vol., 519).—Cinnamic methyl- and ethyl-anilides and diphenylamide react quantitatively, like the diethylamide (*loc. cit.*), with organo-magnesium halides to give after hydrolysis the corresponding amides of β-substituted β-phenylpropionic acids, and a cheaper route to these acids is thus provided. *Cinnamic methylanilide*, m. p. 70°, b. p. 231°/15 mm., *ethylanilide*, m. p. 46°, b. p. 234°/15 mm., and diphenylamide, m. p. 150°, are prepared from cinnamoyl chloride and the appropriate amines. By their interaction with magnesium ethyl and phenyl bromides the following compounds are obtained: β-*phenylvaleric methylanilide*, b. p. 206°/12 mm. (free acid, m. p. 66°), *ethylanilide*, b. p. 244°/15 mm., and *diphenylamide*, m. p. 52—53°, b. p. 265°/18 mm.; ββ-*diphenylpropionic methylanilide*, b. p. 261°/13 mm. (free acid, m. p. 155°), *ethylanilide*, b. p. 278°/25 mm., and *diphenylamide*, m. p. 130°. Magnesium methyl iodide, on the other hand, reacts only slowly with the cinnamic anilides, addition taking place at the carbonyl group with elimination of amine and production of styryl methyl ketone. C. Hollins.

Addition of halogens to unsaturated acids and esters. I. Addition of equimolecular mixtures of bromine and chlorine to cinnamic acid and its derivatives in non-hydroxylic solvents. N. W. Hanson and T. C. James (J.C.S., 1928, 1955—1960).—An equimolecular mixture of bromine and chlorine, dissolved in carbon tetrachloride, reacts additively with cinnamic acid, behaving as a solution of hypothetical bromine monochloride. Two acids are obtained and these are shown, by analysis and by their reactions with two equivalents of methyl-alcoholic potassium hydroxide, to be the two stereoisomeric β-chloro-α-bromo-β-phenylpropionic acids, analogous with cinnamic acid dihalides (higher-melting) and *allo*-dihalides (lower-melting), respectively. The higher-melting acid (I) has m. p. 182° (Erlenmeyer, A., 1896, i, 302). allo-β-*Chloro*-α-*bromo*-β-*phenylpropionic acid* (II) has m. p. 75°. When treated with methyl-alcoholic potassium hydroxide, the acid (I) evolved 39% by weight of the available hydrogen bromide, and 61% of the available hydrogen chloride, the product of this elimination being a mixture of acids from which α-bromo-, α-bromo-*allo*-, and β-chloro-*allo*-cinnamic acids were isolated. The acid (II) evolved 15% of hydrogen bromide and 84% of hydrogen chloride, the only product isolated being α-bromocinnamic acid. The isomeric α-chloro-β-bromo-β-phenylpropionic acid (Erlenmeyer, *loc. cit.*), m. p. 184·5°, evolved hydrogen bromide only, to the extent of 95% by weight of the available amount. Kinetic experiments showed that "bromine chloride" solution reacts with cinnamic acid much more rapidly than either of the halogens separately and with α-methylcinnamic, α-bromo-*o*-methoxycinnamic, and *m*-methoxycinnamic acids and methyl *o*-methoxy-, *o*-methoxy-*iso*-, and *m*-methoxy-cinnamates much more rapidly than bromine alone. M. Clark.

Influence of substituents in the benzene nucleus on mode of reaction of silver salts of *o*-hydroxycarboxylic acids with acetobromoglucose. K. Josephson (Annalen, 1928, 464, 227—236).—An investigation of the effect of the grouping R on the reaction between the silver salt of a substituted salicylic acid and acetobromoglucose. This reaction (cf. Karrer and co-workers, A., 1921, i, 260) may take either or both of two courses, (I) and (II): (I) $OH\cdot C_6H_3R\cdot CO_2Ag+Br\cdot C_6H_7O_5Ac_4 \longrightarrow AgBr+OH\cdot C_6H_3R\cdot CO_2\cdot C_6H_7O_5Ac_4$;
(II) $AgO\cdot C_6H_3R\cdot CO_2H+Br\cdot C_6H_7O_5Ac_4 \longrightarrow AgBr+CO_2H\cdot C_6H_3R\cdot O\cdot C_6H_7O_5Ac_4$. The three silver salts having R=H, R=Me in position 4 and R=Me in position 5 all react according to courses (I) and (II), whilst the three silver salts having R=Me in position 3, R=NO_2 in position 3, and R=NO_2 in position 5 all react in accordance with course (I) only (cf. Josephson, Arkiv Kemi, Min., Geol., 1927, 9, No. 36). It would therefore appear that a 3-methyl or a 3- or 5-nitro-group hinders salt formation of the type suggested by Karrer (*loc. cit.*). Silver 4 : 5-dimethoxysalicylate reacts only along the lines of (I).

Tetra-acetylglucose m-*hydroxytoluate* has m. p. 151°, $[\alpha]_D^{20}$ −46·5°. The corresponding glucoside, *tetra-acetylglucosido*-m-*hydroxytoluic acid*, has m. p. 145°, $[\alpha]_D^{20}$ −28·3°, and is hydrolysed by barium hydroxide solution to β-*glucosido*-m-*hydroxytoluic acid*, m. p. 142°, $[\alpha]_D^{20}$ −56·2°.

Tetra-acetylglucose 3-*nitrosalicylate*, m. p. 140°, has $[\alpha]_D^{20}$ −42·8° (*acetate*, m. p. 145°, $[\alpha]_D^{20}$ −73·5°). *Tetra-acetylglucose* 5-*nitrosalicylate*, m. p. 174°, $[\alpha]_D^{20}$ −47·2°, forms an *acetate*, m. p. 166°, $[\alpha]_D^{20}$ −44·3°. All rotations are for chloroform solutions. E. E. TURNER.

Chaulmoogroyl derivatives of lactates and salicylates. S. SANTIAGO and A. P. WEST (Philippine J. Sci., 1928, **35**, 405—409).—Chaulmoogroyl chloride (*ibid.*, 1927, **33**, 265) reacts with hydroxy-esters to give *methyl* and *ethyl chaulmoogroyl-lactates*, m. p. 51—54° and 54—57°, respectively, *ethyl* and *butyl chaulmoogroylsalicylates*, m. p. 48—51° and 49—50°, respectively, and the corresponding *methyl*, *phenyl*, *amyl*, and iso*amyl* esters, all unstable, decomposing at about 40°. E. W. WIGNALL.

Catalytic reduction of hydroxybenzoic acids. F. BALAŠ and A. KOSIK (Časopis Českoslov. Lék., 1927, 7, 118—121, 136—138, 191—192; Chem. Zentr., 1928, i, 1173).—Reduction of aqueous salicylic acid by hydrogen and colloidal platinum at 60° yields finally *cyclo*hexanol in 50% yield. Similarly, *m*- and *p*-hydroxybenzoic acids yield hexahydro-*m*- and -*p*-hydroxybenzoic acids, respectively.
A. A. ELDRIDGE.

***ortho*-Effect and reactivity. I. Magnitude and cause of the *ortho*-effect in the hydrolysis of aromatic esters.** K. KINDLER [with K. G. ELLINGER].—See this vol., 962.

Condensation product of salicylic acid and *iso*valeric anhydride. J. DALIETOS (Arch. Pharm., 1928, **266**, 325—328).—The *iso*valeryl analogue of acetylsalicylic acid, which should have interesting physiological properties, is not formed by treating a salicylate with *iso*valeryl chloride, nor by heating salicylic acid and *iso*valeric anhydride at atmospheric or higher pressure, for here extensive decomposition, if anything, takes place. When, however, the anhydride and salicylic acid are heated at 150° in presence of a small quantity of sulphuric acid, iso*valerylsalicylic acid*, m. p. 225° (*sodium* salt, m. p. 233—236°), is formed. W. A. SILVESTER.

Catalytic reduction of mandelic acids. K. W. ROSENMUND and H. SCHINDLER (Arch. Pharm., 1928, **266**, 281—283).—When benzyl benzoate is reduced in boiling xylene solution by hydrogen and palladium, toluene and benzoic acid are produced (Rosenmund and Heise, A., 1921, ii, 631). The esters of other alcohols do not similarly give the corresponding hydrocarbon, at least only those which can be regarded as substituted benzyl alcohols in containing an α-phenyl group. Acetylmandelic acid, *i.e.*, α-carboxybenzyl acetate, is similarly smoothly reduced to acetic acid and phenylacetic acid (yield 20% in boiling xylene, 60% in boiling tetralin). *p*-Methoxy- and *o*-chloro-phenylacetic acids are similarly obtained from the acetates of the corresponding mandelic acids. The diacetyl derivative of *o*-hydroxymandelic acid gives directly *o*-hydroxyphenylacetic acid, the *o*-acetyl group being simultaneously removed, in the form of acetaldehyde. The method affords a ready means of obtaining substituted phenylacetic acids.
W. A. SILVESTER.

Chemical constitution and pungency. Syntheses of ethyl hydroferulate [β-4-hydroxy-3-methoxyphenylpropionate] and β-4-hydroxy-3-methoxyphenylpropyl alcohol. H. NOMURA and S. HOTTA (Sci. Rep. Tôhoku Imp. Univ., 1928, **17**, 693—694).—*Ethyl* β-4-*hydroxy*-3-*methoxyphenylpropionate*, b. p. 192·5—193°/17 mm., was prepared by esterification of the acid with alcohol and sulphuric acid. Reduction by sodium and alcohol yielded γ-4-*hydroxy*-3-*methoxyphenylpropyl alcohol*, b. p. 196°/16 mm. The acid, ester, and alcohol are all pungent. R. K. CALLOW.

Attempted synthesis of isomerides of piperic acid. H. LOHAUS (J. pr. Chem., 1928, [ii], **119**, 235—271).—An attempt to synthesise chavicic and *iso*chavicic acids, the $\Delta^{\alpha\beta}$-*cis*-, $\Delta^{\gamma\delta}$-*cis*- and $\Delta^{\alpha\beta}$-*trans*-$\Delta^{\gamma\delta}$-*cis*-isomerides of piperic acid, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$ (cf. Ott and others, A., 1922, i, 1026; 1924, i, 418), could not be based on direct methods, as in these the *cis*- would invert to the *trans*-compounds (cf. the formation of *trans*-cinnamoyl chloride by the action of thionyl chloride on *allo*cinnamic acid; G. MAAS, unpublished). Hydrogenation of an acetylenic compound would, however, be expected to furnish first the less stable product. Accordingly the hydrogenation of *piperonylpropargylidenemalonic acid* has been investigated.

Phenylpropargylidenemalonic acid is prepared by condensing phenylpropargylaldehyde diethylacetal with malonic acid, filtering, and adding sulphuric acid to the mother-liquor; contrary to the statement of Driessen (Diss., Kiel, 1898), the acid is soluble in dilute sodium hydroxide solution without decomposition. Its *pyridine* salt, decomp. 114—116° (from alcohol), is soluble in water which contains pyridine.

The starting-material for the preparation of the piperonyl analogue was 3 : 4-methylenedioxycinnamic acid, obtained in improved yield by eliminating carbon dioxide from piperonylidenemalonic acid in a vacuum. The dibromide was then prepared, and thence 3 : 4-methylenedioxy-ω-bromostyrene. From this, piperonylacetylene was obtained with constant b. p. 103°/11 mm.; the action of magnesium ethyl bromide then furnished the corresponding *magnesyl bromide*, which was treated with ethyl orthoformate in an ether–benzene mixture to give, after addition of sulphuric acid, *piperonylpropargylaldehyde diethylacetal*, b. p. 188—190°/16 mm. (decomp. during isolation), with resinous products and some bispiperonyldiacetylene.

Magnesium piperonylacetylenyl bromide and ethyl formate in ether at −20° gave, after addition of sulphuric acid, the original acetylene and *piperonylpropargylaldehyde*, m. p. 76°, b. p. 159—160°/15 mm., with, under some conditions, an unknown *substance*, m. p. 220°. The aldehyde was also obtained by hydrolysing the above acetal with very dilute sulphuric acid; decomposition accompanied the hydrolysis. The aldehyde could be prepared from the acetylene by means of the *sodium* derivative only by use of a solution of sodium in liquid ammonia: it did not, however, react with ethyl formate.

Piperonylpropargylidenemalonic acid, brown, m. p. 250° (decomp.), was obtained from the acetal and malonic acid in acetic acid, in best yield by using the crude product from the acetylene, without distillation. The yellow *dipyridine* salt, decomp. 231°, when treated with dilute hydrochloric acid yielded a *monopyridine* salt, m. p. 204°, yellow, which on keeping with water was converted into a red *form*, m. p. 237°.

The preparation of 3 : 4-methylenedioxycinnamaldehyde (piperonylacraldehyde) (Ladenburg and Scholtz, A., 1895, i, 42; Winzheimer, A., 1908, i, 656) was repeated, and the m. p. 77—78°, b. p. 175—190°/1 mm., obtained. A *by-product*, m. p. 100—105°, gave with *p*-nitrophenylhydrazine a *compound*, m. p. 258°. From the aldehyde and malonic acid, piperonylidene-ethylidenemalonic acid (Scholtz, A., 1895, i, 468), new m. p. 231—232° (decomp.) (*pyridine* salt, decomp. 191—192°), was prepared.

Catalytic hydrogenation of phenylpropargylaldehyde diethylacetal, employing palladium adsorbed on charcoal, yielded only *trans*-cinnamaldehyde diethylacetal, identified by condensation with malonic acid; the free aldehyde gave similar results. Piperonylpropargylaldehyde yielded oily products; piperonylacraldehyde was reduced to piperonylpropane. Phenylpropargylidenemalonic acid gave in methyl alcohol an oily product, in acetic acid an oil regarded as *cis-cis*-cinnamylideneacetic acid, with some cinnamylidenemalonic acid; the sodium salt yielded an oily product, and the pyridine salt a *cis*-cinnamylidenemalonic acid, decomp. about 106°, which was also obtained, in less pure condition, when palladium adsorbed on barium sulphate was employed.

From piperonylpropargylidenemalonic acid, amorphous products were obtained: it is thought that carbon dioxide was lost. The products from the pyridine and piperidine salts were also unsatisfactory; from the last, *trans*-piperonylethylidenemalonic acid could be obtained. A small quantity of a product regarded as the *cis*-form was obtained, and was heated; carbon dioxide was lost, and a resinous mass obtained, from which an amorphous substance, m. p. 160° (possibly impure *iso*chavicic acid), was separated by extraction with benzene.

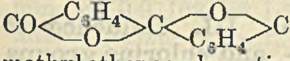
The preparation of *iso*piperic acid (Ott, Eichler, and Heimann, A., 1922, i, 1027) was repeated. Piperonylidene-ethylidenemalonic acid was heated with quinoline at 160°: the product had m. p. 155° (softens 145°). *iso*Piperic acid with thionyl chloride gave piperoyl chloride, identified by conversion into piperic acid, and, by piperidine, into piperin. *iso*Chavicic acid, on the other hand, undergoes no inversion when treated with thionyl chloride. E. W. Wignall.

Sensitive differentiation of phthalic and terephthalic acids. R. Ripan (Bul. Soc. Stiinte Cluj, 1927, 3, 308—310; Chem. Zentr., 1927, ii, 2466).—On treatment of a fairly concentrated solution of a copper salt with the acid in 2% aqueous solution in presence of pyridine, terephthalic acid gives an immediate precipitate of the compound $[C_6H_4(CO_2)_2][Cu(H_2O)_3(C_5H_5N)_3]$, whereas phthalic acid yields a precipitate of the compound $[Cu(C_5H_5N)_2][C_6H_4(CO_2)CO_2H]_2$ only after some hours; the test is very sensitive. The cobalt salts differ even more markedly in solubility.

A. A. Eldridge.

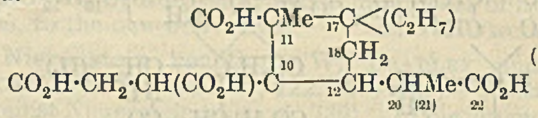
Hydrolysis of esters by solid alkali hydroxides. E. Tassilly, A. Belot, and M. Descombes (Compt. rend., 1928, 186, 1846—1848).—The method of hydrolysis of ethyl phenylethylmalonate by solid alkali hydroxides (this vol., 290) has been extended. The ester is added, with shaking, to finely-powdered potassium hydroxide (2 mols. for each carboxyl group) in a covered crucible; the mass gradually solidifies and the heat generated has occasionally to be controlled. The reaction is generally finished after 1 hr. Solid esters usually react only above their m. p., although methyl oxalate reacts energetically in the cold. Ethyl acetate and the esters of benzoic, phenylacetic, hydrocinnamic, cinnamic, and salicylic acids react in the cold, but methyl cinnamate must be heated at 100°, and likewise the esters of *o*-, *m*-, and *p*-nitrobenzoic acid. The yields of acid are quantitative. The difficultly hydrolysable methyl *allo*camphorate yields camphoric acid quantitatively at 200° by this method. J. D. Fulton.

Molecular configurations of polynuclear aromatic compounds. VII. 5 : 5′-Dichlorodiphenyl-3 : 3′-dicarboxylic acid. F. B. McAlister and J. Kenner (J.C.S., 1928, 1913—1916).—No diphenyl derivative could be prepared from the *ethyl* ester, m. p. 59—60°, of 5-*iodo*-3-*nitrobenzoic acid*, m. p. 166—167°, which is obtained by successive treatment of 3-nitro-5-aminobenzoic acid with potassium metabisulphite in fuming nitric acid and a solution of iodine in potassium iodide. 3-*Bromo*-5-*iodotoluene* (I), prepared from 5-bromo-*m*-toluidine, has m. p. 23°, b. p. 150°/29 mm. 3-*Bromo*-5-*acetamidobenzoic acid*, m. p. 279—281°, obtained by oxidation of 5-*bromoaceto*-m-*toluidide*, m. p. 171—172°, with an aqueous solution of potassium permanganate and hydrated magnesium sulphate, is successively converted into 3-*bromo*-5-*aminobenzoic acid*, m. p. 220—222° (*hydrochloride*), and 3-*bromo*-5-*iodobenzoic acid*, m. p. 209—211° [*methyl* ester (II), m. p. 59—61°]. When either (I) or (II) was heated with copper powder, bromine as well as iodine was eliminated, so that no definite diphenyl derivative could be prepared in either case. 3-*Chloro*-5-*iodotoluene*, m. p. 0°, b. p. 138—140°/26 mm., from 5-chloro-*m*-toluidine, is readily converted when heated with copper powder into 5 : 5′-*dichloro*-3 : 3′-*ditolyl*, m. p. 101—102°. Oxidation failed to yield the corresponding dicarboxylic acid. 3-*Chloro*-5-*acetamidobenzoic acid*, m. p. 265—267°, is converted into 3-*chloro*-5-*aminobenzoic acid hydrochloride*, m. p. 118—121°, and thence by successive treatment with potassium metabisulphite in fuming nitric acid and a solution of iodine in potassium iodide, into 3-*chloro*-5-*iodobenzoic acid*, m. p. 190—191° [*methyl* ester (III), m. p. 43—44°]. When (III) is heated with copper powder, *methyl* 5 : 5′-*dichlorodiphenyl*-3 : 3′-*dicarboxylate*, m. p. 156°, is obtained. 5 : 5′-*Dichlorodiphenyl*-3 : 3′-*dicarboxylic acid*, m. p. 358—360°, yields a *brucine* salt, m. p. 178—179°, decomp. 191—193°, $[\alpha]_D$ —5·2° in chloroform, a *quinine* salt, m. p. 170—172°, decomp. 174°, $[\alpha]_D$ —132° in alcohol, and an *acid morphine* salt, m. p. 218—219°, decomp. 223—225°, $[\alpha]_D$ —30° in alcohol. The solutions of ammonium 5 : 5′-dichlorodiphenyl-3 : 3′-dicarboxylate prepared from these salts were in each case optically inactive. The acid therefore does not exhibit the asymmetry of its 2 : 2′-6 : 6′-structural isomeride (cf. A., 1926, 518). M. CLARK.

Action of phthaloyl chloride on *m*-methoxybenzoic acid and *m*-tolyl methyl ether. R. WEISS and W. KNAPP (Monatsh., 1928, 50, 10—15).—From *m*-methoxybenzoic acid or its methyl ester, phthaloyl chloride, and aluminium chloride there is obtained the *dilactone* of dihydroxy-4-methoxydiphenylmethane-2 : 2′-dicarboxylic acid,  $CO<\frac{C_6H_4}{O}>C<\frac{O}{C_6H_4}>CO$, m. p. 183°. With *m*-tolyl methyl ether condensation occurs *ortho* to the methoxyl group, giving 3′ : 3″-*dimethoxydi*-p-*tolylphthalide*, which is reduced by sodium amalgam in methyl alcohol to 2′ : 2″-*dimethoxy*-4′ : 4″-*dimethyltriphenylmethane*-2-*carboxylic acid*, m. p. 170° (+0·75MeOH; *compound* with 0·25CHCl:CHCl, and *potassium* salt described). Oxidation of this phthalin with alkaline permanganate gives 2 : 2′-*dimethoxytriphenylmethane*-4 : 4′ : 4″-*tricarboxylic acid* (*methyl* ester, *sodium* and *potassium* salts described), which is converted by zinc chloride at 200° into 1 : 2′-*dimethoxy*-9-*phenylanthrone*-3 : 4′-*dicarboxylic acid* (decomp. 250°). C. HOLLINS.

Complex anions of meconic and quinic acid with heavy metals. R. WEINLAND and H. FRIEDE (Arch. Pharm., 1928, **266**, 353—366).—By adding aqueous ferric chloride to a methyl-alcoholic solution of meconic acid and then sodium hydroxide, ammonia, or an organic base in calculated amount (short of alkaline reaction), or by adding aqueous ferric acetate to an aqueous solution of meconic acid containing excess of sodium acetate or to an aqueous solution of meconic acid in sodium hydrogen carbonate, guanidine, or piperidine containing acetic acid, crystalline salts (usually red to brown) of tribasic ferridimeconic acid are obtained. The following are described: *trisodium* salt, $[Fe\{O\cdot C_5HO_2(CO_2)_2\}_2]Na_3,10H_2O$; *triguanidine* salt, $+6H_2O$; *tripiperidine* salt, $+5H_2O$; *ammonium dihydrogen* salt, $+5H_2O$; *monopyridine dihydrogen* salt, $+5H_2O$; *monoguanidine* salt, $+5H_2O$; *monoquinoline* salt, $+6H_2O$; also a *sodium* and a *pyridine* salt in which 4 mols. of acid are present to 7 of base, $+20H_2O$. A green *pyridine chlorochromidimeconate*, $[Cr\{O\cdot C_5HO_2(CO_2)_2\}_2Cl]H_4,C_5H_5N,7H_2O$, is obtained in small yield by adding pyridine to an aqueous methyl-alcoholic solution of meconic acid and green chromic chloride hexahydrate. From a solution of copper sulphate and meconic acid, excess of ammonia precipitates a blue *hexammonium tricupridimeconate*, $+8H_2O$; the green *pyridine* salt contains only 4 mols. of base; a corresponding white *tetrammonium trizincidimeconate* ($+8H_2O$) is described. Quinic acid [1 : 2 : 4 : 5-tetrahydroxy*cyclo*hexane-1-carboxylic acid], although it contains no benzene ring and gives no coloration with ferric salts, yields green *tripotassium* and *trirubidium ferritriquinates*, $[Fe\{O\cdot C_6H_7(OH)_3CO_2\}_3]M_3,12H_2O$. C. HOLLINS.

Bile acids. XXVIII. Nature of the fourth ring. H. WIELAND and F. VOCKE (Z. physiol. Chem., 1928, **177**, 68—85; cf. Wieland, Schlichting, and Jacobi, A., 1927, 247).—Oxidation of the tetracarboxylic acid, $C_{16}H_{24}O_8$ (Wieland and Schlichting, A., 1924, i, 857), with 6% hydrogen peroxide gives, in addition to much acetic acid, acetaldehyde and acetone. Since β-methyladipic and α-methylglutaric acids similarly yield acetone, this is in keeping with the suggested structure (I) for the tetracarboxylic acid.

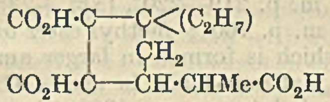


(I.)

The mother-liquors from the preparation of this acid (residues from working-up of 10 kg. of deoxycholic acid) contain succinic acid, α-methylglutaric acid, and an *acid*, $C_7H_{10}O_6$, m. p. 134°, which is not identical with *cis*-α-methyltricarballylic acid, but which by decarboxylation yields α-methylglutaric acid. An identical acid is obtained by hydrolysis of Auwers' ethyl butane-αγγ-tricarboxylate (A., 1896, i, 642). It is concluded that the C_{11} atom in cholanic acid carries a methyl group.

The tetracarboxylic acid gives a trimethyl ester, m. p. 100°, a *triethyl* ester, m. p. 108°, a *dimethyl* ester, m. p. 167°, by esterification, and a *monomethyl* ester, m. p. 163° (*potassium* salt described), by hydrolysis of the tetramethyl ester (*loc. cit.*); hydrolysis of the trimethyl ester, on the other hand, regenerates the free acid. Oxidation with chromic acid of the product of the action of magnesium phenyl bromide on the trimethyl ester gives an *acid*, $C_{28}H_{30}O_4$, m. p. 226—227°; from the tetramethyl ester an isomeric *acid*, m. p. 155°, is similarly obtained.

The *methyl ester trihydrazide*, $C_{17}H_{32}O_5N_6$, m. p. 145° ($+H_2O$; decomp.), prepared from the tetramethyl ester, gives by the Curtius reaction the *trihydrochloride* of a *triamino-acid*, $C_{13}H_{27}O_2N_3,3HCl$, m. p. 250° (decomp.), the oxidation of which by hypochlorous or hypobromous acid gave no useful result.



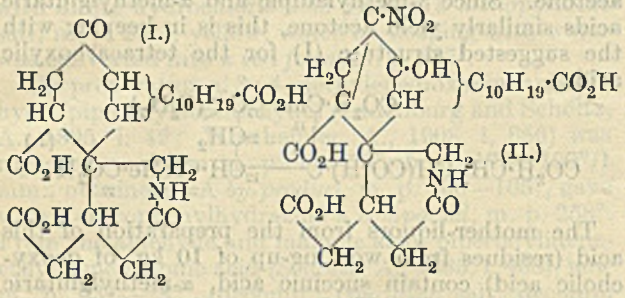
(II.)

The tricarboxylic acid, $C_{13}H_{20}O_6$ (II), obtained by oxidation of the pyro-acid, $C_{15}H_{22}O_5$ (*loc. cit.*), yields by the usual esterification method only a *dimethyl* ester, b. p. 208—210°/1 mm., which is converted by diazomethane into the *trimethyl* ester, b. p. 170° in high vacuum. The *methyl ester dihydrazide* from this gives by the Curtius reaction a *diamino-acid*, decomp. 280°.

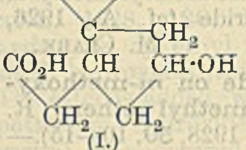
In the preparation of pyrodeoxybilianic acid by thermal decomposition of deoxybilianic acid a stereoisomeric "β"-*deoxybilianic acid*, m. p. 221—222°, is obtained as a by-product; it is possibly an intermediate in the conversion into the pyro-acid. C. HOLLINS.

Bile acids. XX. Nitrogenous derivatives of bilianic acid. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1928, **176**, 187—199; cf. this vol., 764).—The white compound, $C_{24}H_{35}O_8N$, precipitated by acids from the alkaline solution of the blue nitroso-compound obtained from bilianic acid di*iso*oxime (*loc. cit.*) is a tricarboxylic acid (I) formed by exchange of hydroxyl for the nitroso-group, probably followed by ketonisation. It exists in two forms, (*a*) small crystals, m. p. 200—205° (decomp.; sintering at 185°), containing H_2O, and (*b*) needles, m. p. 260° (decomp.; anhydrous). Under similar conditions bilianic acid dioxime gives a blue *nitroso*-compound, $C_{24}H_{33}O_8N$, m. p. 236—238° (decomp.; sinters at 220—230°), which by the action of alkali yields bilianic acid [as (I) with omission of the NH]. The substance (I) is also obtained by oxidation of bilianic di*iso*oxime with permanganate. Oxidation of the di*iso*oxime or of the blue nitroso-compound therefrom with nitric acid (*d* 1·4) at 15° yields a hydroxytricarboxylic *acid*, $C_{24}H_{24}O_{10}N_2$, m. p. 212—214° (decomp.), of probable structure (II).

C. HOLLINS.


(I.) (II.)

Bile acids. XIII. Catalytic reduction of ketonic acids of the bile acid group. W. BORSCHE and E. FESKE (Z. physiol. Chem., 1928, **176**, 109—121; cf. Borsche and Frank, A., 1926, 1140).—By means of an exceptionally active platinum-black catalyst dehydrocholic acid, m. p. 237—238°, is reduced with hydrogen in glacial acetic acid to 3 : 7 : 12-trihydroxycholanic acid, m. p. 196—197°, $[\alpha]_D^{20}$ +35·91° in alcohol (identical with that of natural cholic acid); the previously recorded high rotation is probably due to the presence of *dihydroxyketocholanic acid*, m. p. 219—220°, $[\alpha]_D^{20}$ +73° in alcohol (*methyl* ester, m. p. 160°; methyl ester *oxime*, m. p. 111—112°), which is formed in larger amount when a less active platinum-black is used. Oxidation of methyl deoxycholate, m. p. 130° (the m. p. and rotation given by Borsche and Frank are erroneous), with chromic acid yields the dehydro-ester together with *methyl hydrogen deoxybilianate*, $C_{19}H_{27}O_5{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me$, m. p. 278°. Dehydrodeoxycholic acid, m. p. 189°, is reduced to deoxycholic acid, m. p. 141—143° (+AcOH), $[\alpha]_D^{20}$ +49·33°, identical with the natural product, whilst bilianic acid yields reductobiliobanic acid, m. p. 243° (Windaus and van Schoor, A., 1926, 169; *methyl* ester, m. p. 135°), which is oxidised by chromic acid to biliobanic acid, m. p. 307°. The reduction of deoxybilianic acid to 7-*hydroxylithobilianic acid*, m. p. 269—271° (*trimethyl* ester, m. p. 105°), of pyrodeoxybilianic acid to the corresponding *dihydroxy-acid*, $C_{23}H_{38}O_4$, m. p. 211—213° (*methyl* ester, m. p. 168°), and of *iso*bilianic acid to reducto*iso*biliobanic acid, m. p. 278°, is described. The last-mentioned acid is converted by warm alkali into 7 : 12-*dihydroxylithobilianic acid*, melting and decomposing at 162° with regeneration of the lactonic acid, m. p. 278°. Reducto*iso*biliobanic acid is oxidised by chromic or nitric acid to *iso*biliobanic acid, m. p. 264—265° [*oxime*, m. p. 215°; dimethyl ester, m. p. 172°; dimethyl ester oxime, m. p. 188° (decomp.)]. Reductobiliobanic acid and 7-hydroxylithobilianic acid, which both contain the grouping (I), show no tendency to δ-lactone formation; it is not safe, however, to conclude from this that reducto*iso*biliobanic acid has a γ- rather than a δ-lactone bridge.


(I.)

C. HOLLINS.

Colour and constitution. III. Influence of the methylthiol, methoxy-, and chlorine groups on the colours of the nitrobenzaldehydephenylhydrazones. H. H. HODGSON and F. W. HANDLEY (J.C.S., 1928, 1882—1886).—The influence of the methylthiol, methoxy-, and chlorine groups on the colours of certain nitrobenzaldehydephenylhydrazones containing these substituents in the *ortho*- and *para*-positions in the benzaldehyde and phenylhydrazine residues, respectively, is investigated. Equimolecular alcoholic solutions exhibit a well-defined order which is the same whether the groups are present in the aldehyde or hydrazine residue and is independent of the position of the nitro-group in the remaining residue, viz., *o*-Cl (lemon-yellow), *o*-SMe, *p*-Cl, H, *o*-OMe, *p*-SMe (increasing depth), *p*-OMe (deep reddish-orange). The absorption spectra curves of the *p*-nitrobenzaldehydephenylhydrazones confirm the results of the visual observations. The influence of the substituents is, in general, less marked than in the case of the azo-dyes (cf. this vol., 284). *p*-Nitrobenzaldehydephenylhydrazone, already shown to exist in two polymorphic forms (Ciusa and Vecciotti, A., 1911, i, 810), crystallises from glacial acetic acid in yellow needles, m. p. 194°, which slowly change to a pale orange modification of unchanged m. p. Exposure to ultra-violet light is without effect. Addition of water to a solution of the substance in glacial acetic acid precipitates a yellow variety changing in a few seconds into the red form of Ciusa and Vecciotti. Attempts to prepare *o*-methylthiolbenzaldehyde were unsuccessful. The following are described: 4-*methylthiolphenylhydrazine*, m. p. 60° (*hydrochloride*), obtained by reduction of the diazonium compound from 4-thioanisidine hydrochloride; 2-*methylthiolphenylhydrazine*, m. p. 40°, similarly prepared from 2-thioanisidine hydrochloride (an amorphous by-product, m. p. below 100°, was also obtained); o- and p-*chlorobenzaldehyde*-o-*nitrophenylhydrazones*, m. p. 178° and 203—204°; o- and p-*methoxybenzaldehyde*-o-*nitrophenylhydrazones*, m. p. 176—177° and 204°; p-*methylthiolbenzaldehyde*-o-*nitrophenylhydrazone*, m. p. 225—226°; o- and p-*chlorobenzaldehyde*-m-*nitrophenylhydrazones*, m. p. 171° and 172°; o- and p-*methoxybenzaldehyde*-m-*nitrophenylhydrazones*, m. p. 176° and 156°; p-*methylthiolbenzaldehyde*-m-*nitrophenylhydrazone*, m. p. 146°; p-*chlorobenzaldehyde*-p-*nitrophenylhydrazone*, m. p. 224°; o-*methoxybenzaldehyde*-p-*nitrophenylhydrazone*, m. p. 204—205°; p-*methylthiolbenzaldehyde*-p-*nitrophenylhydrazone*, m. p. 183°; o-*nitrobenzaldehyde*-o- and -p-*methylthiolphenylhydrazones*, m. p. 87—88° and 204°; m-*nitrobenzaldehyde*-o- and -p-*methylthiolphenyl*-

hydrazones, m. p. 118° and 152°; p-*nitrobenzaldehyde*-o- and -p-*methylthiolphenylhydrazones*, m. p. 147° and 179°; *benzaldehyde*-p-*methylthiolphenylhydrazone*, m. p. 93°; p-*methylthiolbenzaldehydephenylhydrazone*, m. p. 138°. M. CLARK.

Condensation of heptaldehyde with aromatic aldehydes. B. N. RUTOWSKI and A. I. KOROLEW (J. pr. Chem., 1928, [ii], **119**, 272—274).—Heptaldehyde and benzaldehyde in aqueous alcohol condense under the influence of sodium hydroxide to give β-*phenyl*-α-*amylacraldehyde*, b. p. 174—175°/20 mm., d_{20}^{20} 0·97108, n^{20} 1·5381, of pleasant odour when diluted (*oxime*, m. p. 72·5—73°; *semicarbazone*, m. p. 117·5—118°). This further condenses with benzoylglycine to give 2-*phenyl*-4-β-*benzylideneheptylidene*-5-*oxazolone*, m. p. 97—98°. E. W. WIGNALL.

Physical properties of salicylaldehyde. T. S. CARSWELL and C. E. PFEIFER (J. Amer. Chem. Soc., 1928, **50**, 1765—1766).—Purification of a sample, f. p. —7° (the accepted value), by vacuum fractionation, conversion into the hydrogen sulphite compound, and redistillation, gives pure salicylaldehyde, f. p. 1·6°, b. p. 196·4—196·5°/751 mm., d_{20}^{20} 1·1690. H. E. F. NOTTON.

Catalytic nuclear hydrogenation of acetals of aromatic and semi-aromatic aldehydes. I. F. SIGMUND (Monatsh., 1928, **49**, 271—282; cf. A., 1927, 1054).—Hydrogenation of phenylacetaldehyde diethylacetal with platinum-black in anhydrous acetic acid yields chiefly a mixture of hexahydrophenylacetaldehyde diethylacetal and unreduced acetal, b. p. 222—230°, together with small quantities of liquids, b. p. 195—202° (chiefly hexahydrophenylethyl ethyl ether) and b. p. 202—210° (probably a mixture of the latter ether and reduced acetal). Phenylacetaldehyde dimethylacetal under similar conditions gives an 81% yield of hexahydrophenylacetaldehyde dimethylacetal (I), b. p. 204·5—206°, and a small quantity of a fraction of b. p. 194—197° (probably a mixture of hexahydrophenylethyl methyl ether and the reduced acetal). Treatment of (I) with sulphuric and acetic acids gives hexahydrophenylacetaldehyde, b. p. 179—182° (semicarbazone, m. p. 162°; cf. Skita, Ber., 1915, 48, 2, 1694), and a small, less volatile fraction probably produced by the slight polymerisation of the aldehyde. I. VOGEL.

Analysis of vanillin and vanillin sugar. J. PRITZKER and R. JUNGKUNZ (Chem.-Ztg., 1928, **52**, 537).—The most suitable qualitative test for vanillin is the mercuric nitrite test of Nickel, as modified by Kreis and Studinger. For gravimetric determination, precipitation with *m*-nitrobenzhydrazide is recommended. A suitable volumetric method consists in titration with 0·1*N*-sodium hydroxide, using thymolphthalein as indicator. S. I. LEVY.

Synthesis of a new [methylated] gallaldehyde. F. MAUTHNER (J. pr. Chem., 1928, [ii], **119**, 306—310).—*Gallaldehyde* 4-*methyl ether* (3 : 5-*dihydroxy*-4-*methoxybenzaldehyde*), m. p. 139—140° (p-*nitrophenylhydrazone*, m. p. 222—223°), is obtained as follows. Methyl gallate is methylated by diazomethane (cf. Herzig and Pollak, A., 1903, i, 89) and the product hydrolysed to gallic acid 4-methyl ether (Graebe and Martz, A., 1903, i, 262); this is treated in alkaline solution with methyl chloroformate, yielding OO′-*dicarbomethoxy*-4-*methoxy*-α-*resorcylic acid*, m. p. 120—121°, of which the acid *chloride*, m. p. 58—59°, is reduced in toluene by hydrogen in the presence of palladium, at 110°, to the corresponding *aldehyde*. The last is hydrolysed by alkali, in presence of hydrogen, to the new derivative. E. W. WIGNALL.

Nierenstein reaction. W. BRADLEY and R. ROBINSON (Nature, 1928, **122**, 130—131).—Polemical against Nierenstein (this vol., 739). In the interaction of diazomethane and benzoyl chloride, the reaction $PhCO{\cdot}Cl+CH_2N_2=PhCO{\cdot}CH_2Cl+N_2$ (*a*) is not the primary action; the reactions $PhCO{\cdot}Cl+CH_2N_2=PhCO{\cdot}CHN_2+HCl$ (*b*) and $HCl+CH_2N_2=CH_3Cl+N_2$ (*c*) are much more rapid than $PhCO{\cdot}CHN_2+HCl=PhCO{\cdot}CH_2Cl+N_2$ (*d*). Hence the observed evolution of nitrogen is a measure of the extent to which the final yield of chloroacetophenone by (*b*) and (*d*) falls short of the theoretical. Under favourable conditions the yield of chloroacetophenone from equimolecular proportions of benzoyl chloride and diazomethane is 9% of the theoretical. It is recommended that the reagents should be mixed as rapidly as possible. A. A. ELDRIDGE.

Degradation of *o*-substituted aromatic acid azides. H. LINDEMANN and W. SCHULTHEIS.—See this vol., 1028.

Sulphur-containing derivatives of acetophenone. E. RIESZ and W. FRANKFURTER (Monatsh., 1928, **50**, 68—75).—By the action of chlorosulphonic acid acetophenone yields a *disulphonyl chloride*, m. p. 195—196° (decomp.), from which the *disulphonanilide*, m. p. 195—196° (decomp.), and dithiolacetophenone, m. p. 128° (*lead* salt described), are obtained. *p*-Aminoacetophenone, diazotised and treated with alkaline xanthate, gives after hydrolysis p-*thiolacetophenone*; this is condensed with chloroacetic acid to give p-*acetophenylthioglycollic acid*, m. p. 155—156°, which by treatment with chlorosulphonic acid is converted into 5 : 5′-diacetothioindigotin. The *p*-thiolacetophenone is oxidised to acetophenone-*p*-sulphonic acid, which on sulphonation with chlorosulphonic acid yields an *acetophenonedisulphonyl chloride*, m. p. 210° (decomp.) [*anilide*, m. p. 235° (decomp.)], which is thus different from the direct sulphonation; it gives on reduction a *dithiolacetophenone*, m. p. 215° (*lead* salt described). C. HOLLINS.

Action of bromine on phenyl β-phenylstyryl ketone. R. BARRÉ and E. P. KOHLER (J. Amer. Chem. Soc., 1928, **50**, 2036—2040).—The results differ from those of previous workers (cf. Dilthey and Last, A., 1916, i, 821; Vorländer, A., 1923, i, 682; Moureu, A., 1923, i, 921). When bromine and phenyl β-phenylstyryl ketone are refluxed together in chloroform *phenyl* α-*bromo*-β-*phenylstyryl ketone*, m. p. 88—89° (rapid heating), is obtained in 90% of the theoretical yield. It is reduced by zinc dust and acetic acid to phenyl ββ-diphenylethyl ketone. If, however, bromination is carried out at the ordinary temperature for 15—20 hrs., the bromo-derivative is partly dehydrated by the hydrogen bromide formed to 1 : 2-*dibromo*-1 : 3-*diphenylindene*, m. p. 104—105°.

This has a reactive bromine atom and forms with alcohol 2-*bromo*-1-*ethoxy*-1 : 3-*diphenylindene*, m. p. 130—131°. It is ozonised to *o*-dibenzoylbenzene.

H. E. F. Notton.

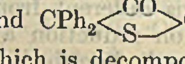
Nitrogen trichloride and unsaturated ketones. II. G. H. Coleman and D. Craig (J. Amer. Chem. Soc., 1928, **50**, 1816—1820).—Solutions of nitrogen trichloride in carbon tetrachloride are conveniently analysed by conversion into ammonium chloride by evaporation with hydrochloric acid in a current of air. Styryl methyl ketone and nitrogen trichloride in carbon tetrachloride (cf. A., 1927, 1190) at —10° form ammonium chloride, αβ-dichloro-β-phenylethyl methyl ketone, which decomposes at the ordinary temperature into β-chlorostyryl methyl ketone, and α-*chloro*-β-*amino*-β-*phenylethyl methyl ketone hydrochloride* (I) (5% of the theoretical yield), m. p. 176—177° (decomp.), which is converted by the Schotten–Baumann method into a *by-product*, m. p. 204°, and a *benzamido*-derivative, m. p. 160—161°. This is reduced by sodium amalgam and alcohol to α-*benzamido*-α-*phenylbutan*-γ-*ol*, m. p. 150—151°. The hydrochloride (I) is reduced similarly to α-*amino*-α-*phenylbutan*-γ-*ol*, m. p. 74—76° (*dibenzoyl* derivative, m. p. 139—141°). β-*Amino*-α-*phenylbutan*-γ-*ol*, m. p. 62—64° (*hydrochloride*, m. p. 114—116°), and β-*benzamido*-α-*phenylbutan*-γ-*ol*, m. p. 177—179°, were prepared for comparison from α-amino-β-phenylethyl methyl ketone (cf. Sonn, A., 1908, i, 55).

H. E. F. Notton.

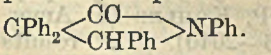
2 : 4 : 7-Trinitrofluorenone. F. Bell (J.C.S., 1928, 1990).—Nitration of fluorenone by the method of Schmidt and Bauer (A., 1906, i, 27) yields, not 2 : 3 : 7-trinitro-, but 2 : 4 : 7-*trinitro-fluorenone*, m. p. 175°, identical with the product obtained by nitration of 4-nitrofluorenone with nitric acid (*d* 1·5) on the steam-bath.

J. W. Baker.

Thiobenzophenone. H. Staudinger and H. Freudenberger [with E. Senn, S. Vendrell, and I. Siegwart] (Ber., 1928, **61**, [*B*], 1576—1583).—The action of benzophenone chloride on potassium sulphide affords a mixture of thiobenzophenone and unchanged benzophenone which can scarcely be separated into its components by fractional distillation. If the product is treated with diphenylketen, the compound



$CPh_2{<}\genfrac{}{}{0pt}{}{CO}{S}{>}CPh_2$, m. p. 180—181°, separates, which is decomposed by distillation with benzylideneaniline in a vacuum into thiobenzophenone, m. p. 54—55°, and the β-lactam,



$CPh_2{<}\genfrac{}{}{0pt}{}{CO}{CHPh}{>}NPh$. The preparation of thiobenzophenone from benzophenone chloride and sodium sulphide suffers under the disadvantage that benzophenone is formed by the action of alkali on the chloride; better results are obtained by the gradual addition of sodium hydrogen sulphide to the chloride dissolved in alcohol in the complete absence of air. The polymeric thiobenzophenone of Siegwart (Diss., Zürich, 1917) is a mixture of sulphur and dibenzhydryl disulphide, m. p. 152—153°. Thiobenzophenone can be prepared in 75% yield by the action of hydrogen sulphide on benzophenone dichloride at 150°; if the reaction is prolonged, the products are sulphur and tetraphenylethylene. The readiest method for the preparation of thiobenzophenone consists in the treatment of benzophenone in alcohol with hydrogen chloride and hydrogen sulphide. Thiobenzophenone forms dark violet needles, m. p. 54—55°, and possibly exists in a polymeric form, m. p. 51°. It is far more reactive than benzophenone, readily undergoing change with diphenylketen and aliphatic diazo-compounds. With aniline and phenylhydrazine it affords benzophenone-anil and -phenylhydrazone, respectively. It does not condense with acetaldehyde, acetone, or ethyl acetate in the presence of tertiary bases, whereas it is decomposed if sodium ethoxide is employed. It does not give an additive compound with triethylphosphine. At 160—170° it yields tetraphenylethylene and sulphur. It readily undergoes auto-oxidation to benzophenone, a little sulphur dioxide and sulphur, and a trisulphide, m. p. 124°. Pure thiobenzophenone does not polymerise if preserved for years and is not affected by addition of pyridine, trimethylamine, triethylphosphine, or hydrogen chloride. It is reduced by sodium sulphide, sodium hydrogen sulphide, ammonium sulphide, or sodium ethoxide in alcoholic solution to dibenzhydryl disulphide, m. p. 152—153°. The last-named compound is prepared in quantitative yield by the action of excess of sodium hydrogen sulphide on benzophenone dichloride. Its constitution is established by its formation from thiobenzhydrol (from hydrogen sulphide and diphenyldiazomethane) and iodine. It is further formed from benzophenone and ammonium sulphide. It is reduced by aluminium amalgam to thiobenzhydrol and converted when heated into thiobenzophenone, diphenylmethane, and sulphur.

H. Wren.

Carvacryl [2-hydroxy-5-*p*-cymyl] ketones. K. W. Rosenmund and C. Wha (Arch. Pharm., 1928, **266**, 407—411).—The following ketones have been prepared from carvacrol by the method used with other phenols by Rosenmund and Schulz (A., 1927, 667): 2-*hydroxy*-5-p-*cymyl methyl ketone*, m. p. 120° (*methyl ether*, b. p. 164°/18 mm.); *ethyl ketone*, m. p. 110°, b. p. 201°/15 mm. (*oxime*, m. p. 145°); *propyl ketone*, m. p. 90°, b. p. 200°/15 mm. (*oxime*, m. p. 120°). The ethyl and propyl ketones are reduced by Clemmensen's method to 5-*propylcarvacrol*, b. p. 150°/14·5 mm., and 5-*butylcarvacrol*, b. p. 158°/12 mm., respectively. 2-Hydroxy-5-*p*-cymyl methyl ketone condenses with benzaldehyde in presence of alkali to give 2-*hydroxy*-5-p-*cymyl* β-*hydroxy*-β-*phenylethyl ketone*, m. p. 158°. The corresponding 2-*methoxy*-compound, m. p. 72°, is similarly prepared. 2-Methoxy-5-*p*-cymyl methyl ketone is also condensed with ethyl mesoxalate, giving after hydrolysis 4-*methoxy*-3-*methyl*-6-iso*propylphenacylmalic acid*, m. p. 96° (*ethyl* ester, b. p. 190°/0·5 mm.), which by decarboxylation at 96—110° is converted into the corresponding *glycollic acid* (*ethyl* ester, b. p. 180—184°/0·36 mm.).

C. Hollins.

Acyl wandering with phenols. K. W. Rosenmund and W. Schnurr (Annalen, 1928, **460**, 56—98).—The synthesis of phenolic ketones by the Behn method (G.P. 95,901, 1897), which was recently improved (A., 1927, 667), is now shown to take place as a result of intermediate ester formation; for, when thymol, acetyl chloride, nitrobenzene, and aluminium chloride are used, thymyl acetate is formed intermediately and may actually be isolated. For the conversion of the ester of a phenol into the ketone, the former is treated with 1·2—1·3 mols. of aluminium chloride in 5 parts of nitrobenzene (1 day in the cold).

It is also shown that the conditions previously used for effecting the Fries transformation are unnecessary. Thus, in the case of the conversion of *p*-tolyl benzoate into 2-hydroxy-5-methylbenzophenone only 1 mol. of aluminium chloride (corrected for purity of the sample used) need be used. Moreover, complete reaction is usually effected by heating the mixture at 120° for 10 min. Details for this "baking" process are given.

The acetyl group in thymyl acetate shows a marked tendency to migrate to the *p*-position with respect to the hydroxyl group. The change occurs in the cold in little more than a day, whilst at 60° it is complete in 10 min. Most aliphatic acyl radicals migrate at about the same rate as the acetyl group. The approximate rates of formation of the following ketones by the nitrobenzene method have been determined: 4-hydroxy-2-methyl-5-*iso*propyl-acetophenone, and the corresponding -propiophenone, -butyrophenone, -*iso*valerophenone, -*octophenone* (m. p. 81—82°, b. p. 217—220°/9 mm.), -*phenylacetophenone* (m. p. 105°), -cinnamophenone, and -β-*phenylpropiophenone*, m. p. 122° (from thymol esters, b. p. as follows: acetate, 131°/21 mm., propionate, 248°/760 mm., butyrate, 265°/760 mm., iso*valerate*, 143°/9 mm., *octoate*, 186°/9 mm., *phenylacetate*, 188°/9 mm., β-*phenylpropionate*, 218°/13 mm.). 4-Hydroxy-5-methyl-2-*iso*propyl-acetophenone (m. p. 120°), and the corresponding -propiophenone, -butyrophenone, and -iso*valerophenone*, m. p. 108°, b. p. 201°/13 mm., are obtained, respectively, from the acetate, b. p. 238°/750 mm., *propionate*, b. p. 250°/760 mm., *butyrate*. b. p. 263°/760 mm., and iso*valerate*, b. p. 271°/760 mm., of carvacrol. Clemmensen reduction of 2-hydroxy-4-methylpropiophenone affords 5-*methyl*-2-*propylphenol*, b. p. 129°/16 mm., the *acetate* (b. p. 124°/14 mm.) of which is very readily converted into 4-*hydroxy*-2-*methyl*-5-*propylacetophenone*, m. p. 113°, b. p. 194°/13 mm.

Aromatic acyl radicals migrate with considerably greater difficulty. From thymyl benzoate and carvacryl benzoate (b. p. 191°/14 mm.), 4-*hydroxy*-2-*methyl*-5-iso*propylbenzophenone*, m. p. 153°, and 4-hydroxy-5-methyl-2-*iso*propylbenzophenone, m. p. 172—173°, are obtained.

The rate of migration of acyl radicals into the *p*-position in the case of thymol esters is given by the order: $\cdot$Ac, $\cdot$COEt and homologues $>\cdot CO\cdot CH_2Ph$, $\cdot CO\cdot [CH_2]_2Ph$, $\cdot CO\cdot CH{:}CHPh > Bz$.

Migration of an acyl group into an *o*-position (the *p*-position being blocked) is markedly less facile than *p*-migration. The migration proceeds rapidly (10 min. at 120°) in absence of nitrobenzene, however. In this way, from *p*-tolyl esters (b. p. as follows: *hexoate*, 142—143°/14 mm., *heptoate*, 168°/17 mm., *octoate*, 175°/12 mm.), the following have been prepared: 2-hydroxy-5-methyl-acetophenone and the corresponding -propiophenone, -butyrophenone, -*iso*valerophenone, -*hexophenone* (b. p. 163°/15 mm.), -*heptophenone* (b. p. 168°/10 mm.), and -*octophenone*, m. p. 36°. From 6-chloro-*m*-tolyl esters (b. p. as follows: *acetate*, 121°/15 mm., *propionate*, 250°/760 mm., *butyrate*, 263°/760 mm.) there are produced the following: 5-*chloro*-2-*hydroxy*-4-*methyl–acetophenone* (m. p. 71—72, b. p. 137°/15 mm.) and the corresponding -*propiophenone* (m. p. 76°) and -*butyrophenone* (m. p. 61—62°).

3-*Chloro*-2-*hydroxy*-5-*methyl*-*acetophenone*, m. p. 91°, has been obtained from 3-*chloro*-p-*tolyl acetate*, b. p. 238°/760 mm., the corresponding -*propiophenone*, m. p. 115°, from the *propionate*, b. p. 248°/760 mm., and the -*butyrophenone*, m. p. 62°, from the *butyrate*, b. p. 260°/760 mm.

Reduction of 4-hydroxy-2-methylacetophenone by Clemmensen's method produces 3-*methyl*-4-*ethylphenol*, b. p. 122°/15 mm., the *acetate* (b. p. 124°/15 mm.) of which is converted into 2-*hydroxy*-4-*methyl*-5-*ethylacetophenone*, m. p. 96—97°, b. p. 142—143°/15 mm., by aluminium chloride. Similarly, the acetate of 2-hydroxy-5-methylacetophenone is readily converted into 3 : 5-diacetyl-*p*-cresol, m. p. 83°, b. p. 194°/13 mm., although the benzoate refuses to undergo a similar change.

Aromatic residues undergo *o*-migration less readily than aliphatic residues. The following have been prepared by heating the appropriate ester for 10 min. at 140° with aluminium chloride: 2-hydroxy-5-methyl-, 2′-*chloro*-2-*hydroxy*-5-*methyl*- (m. p. 78°, b. p. 195°/15 mm.), 2′-*bromo*-2-*hydroxy*-5-*methyl*- (m. p. 76—77°) and 4′-*bromo*-2-*hydroxy*-5-*methyl*- (m. p. 79°, b. p. 210°/14 mm.), 5-*chloro*-2-*hydroxy*-4-*methyl*- (m. p. 142°), and 3-*chloro*-2-*hydroxy*-5-*methyl*-*benzophenone*, m. p. 71°.

Various determinations of relative rates of *o*-migration have been made. True aliphatic radicals migrate more rapidly than the phenylacetyl group, and the benzoyl and bromobenzoyl radicals migrate much less rapidly than the latter.

Although it is known that 2 : 4 : 6-trimethylphenyl esters undergo the Fries change, which is accompanied by displacement of a methyl group by acyl, 2 : 4 : 6-tribromophenol is unaffected under similar conditions.

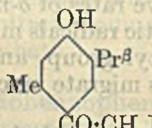
With phenyl esters possessing free *o*- and *p*-positions either migration may take place. Mild conditions favour *p*-migration, drastic conditions *o*-migration. Thus when *m*-tolyl acetate is treated in nitrobenzene with aluminium chloride at 25°, only *p*-migration occurs; at 90—100° approximately equal amounts of *o*- and *p*-change take place, whilst at 165° only *o*-change occurs. Similar results are obtained using *o*-tolyl and *p*-hydroxyacetophenone acetates, and the corresponding homologous esters (propionates to octoates; no details given).

In the case of aromatic residues, temperature again may be used to control the course of the migration. At 165°, *m*-tolyl benzoate is quantitatively converted into 2-hydroxy-4-methylbenzophenone, whilst at lower temperatures the 4 : 2-isomeride is the main product. The other ketones produced in this part of the investigation are *p*-hydroxy- and 4-hydroxy-3-methyl-benzophenone.

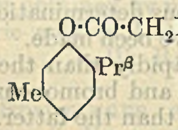
The tendency, present in phenyl esters, for *o*-migration is decreased by introducing (*o*-tolyl esters) a 2-methyl group, but is markedly increased (*m*-tolyl esters) by introducing a *m*-methyl radical (figures given for "baking" in the cases of the acetates and benzoates of the three phenols at 120°). The nitro-group (*o*-nitrophenyl esters) completely inhibits migration, which is also inhibited by an *o*-acyl group. The carboxyl group is inhibiting when in the *m*- or *p*-position with respect to the hydroxyl, but acetylsalicylic acid is convertible into 4-hydroxyacetophenone-3-carboxylic acid. The corresponding benzoate does not give a migration reaction. The action of aluminium chloride on phenyl anisate gives only 4 : 4′-dihydroxybenzophenone.

In an attempt to convert 4-*acetoxy*-2-*methylacetophenone*, b. p. 163°/15 mm. (I), into 5-acetyl-4-hydroxy-2-methylacetophenone (II), there were obtained only 4-hydroxy-2-methyl- (III) and 2-hydroxy-4-methyl-acetophenone (IV). That (II) is not first formed and then converted into (III) and (IV) is shown by the fact that 4-*benzoyloxy*-2-*methylacetophenone*, m. p. 52—53°, passes, under similar conditions, into 2-hydroxy-4-methylacetophenone, no 2-hydroxy-4-methylbenzophenone being produced. The reactions involved are therefore (1) migration of the group in the *p*-position to the *o*-position, and (2) hydrolysis of the ester. That such migration is possible is shown by the conversion, by aluminium chloride at 170°, of (III) into (IV) and by an analogous conversion carried out with the corresponding benzoyl compound (at 180—190°).

When slightly impure 4-hydroxy-2-methyl-5-*iso*propyl*iso*valerophenone (V) is distilled in a vacuum, small quantities of thymyl *iso*valerate (VI) are formed. Although (V) is unaffected in this respect by a large number of acids etc. it is converted to a greater or less extent into (VI) when heated for 2—5 hrs. at 180—250° with sulphuric acid, sulphuryl chloride, phosphoric acid, or camphorsulphonic acid, the last-named being particularly effective. A number of ketones of type (V) have been heated at 150° for 1 hr. with a trace of camphorsulphonic acid. In general, 2-hydroxyphenyl alkyl ketones, 2-hydroxy-3-(4- or -5-)methylphenyl alkyl ketones, 2-hydroxy-5-methyl-3-ethyl-, 2-hydroxy-4-methyl-5-ethyl-, 3-chloro-2-hydroxy-5-methyl-, and 5-chloro-2-hydroxy-4-methyl-phenyl alkyl ketones are not subject to the (V) ⟶ (VI) type of change (*o*-hydroxy-ketones). Yet, whilst 4-hydroxyphenyl alkyl ketones and simply substituted 4-hydroxy-3-methylphenyl alkyl ketones are also stable under the conditions employed, 4-hydroxy-2-methyl-, 4-hydroxy-2-methyl-5-*iso*propyl-, and 4-hydroxy-5-methyl-2-*iso*propyl-phenyl alkyl ketones undergo conversion into esters. The actual cases described are the conversion of 4-hydroxy-2-methylacetophenone into *m*-tolyl acetate, that of 4-hydroxy-2-methylphenacetophenone into *m*-tolyl phenylacetate, those of 4-hydroxy-2-methyl-5-*iso*propyl-aceto-, -propio-, -butyro-, -*iso*valero-, and -benzo-phenones into thymyl acetate, propionate, butyrate, *iso*valerate, and benzoate, respectively, those of 4-hydroxy-5-methyl-2-*iso*propyl-aceto-, -butyro-, and -benzo-phenones into carvacryl acetate, butyrate, and benzoate, respectively, and that of 4-hydroxy-2-methylbenzophenone into *m*-tolyl benzoate.

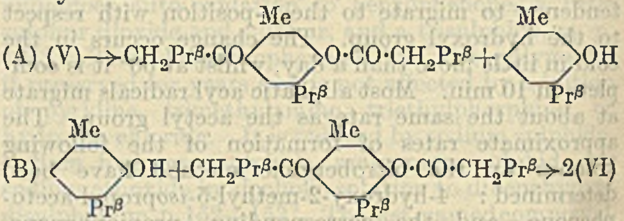


(V.)



(VI.)

When (V) is heated for ½ hr. at 150° in presence of camphorsulphonic acid, thymol, thymyl *iso*valerate (VI), and the iso*valerate*, b. p. 200°/14 mm., of (V) are formed. If the reaction is carried out in a vacuum, so that the thymol is removed as fast as it is formed, the sole other product is the *iso*valerate of (V). If the latter is heated with more thymol and the catalyst, thymyl *iso*valerate results, so that the reactions involved in a normal heating of (V) with catalyst are :



with possibly a second (B′) stage involving interaction of a molecule each of ketone ester with (V).

When a mixture of phenol and 4-*methoxy*-2-*methyl* 5-iso*propylbutyrophenone*, m. p. 50°, is heated with camphorsulphonic acid, the products are thymol methyl ether and phenyl butyrate, further evidence for stage (B) above. The migration of acyl groups from the nucleus to the phenolic oxygen is thus a bimolecular change.

The mechanism of the Fries transformation is discussed. It may be due to formation of acid chloride from the ester, followed by a Friedel–Crafts reaction (Skraup and Poller, A., 1925, i, 143), or it may be (von Auwers) an intramolecular change. That it is not of the latter type is suggested by the fact that simultaneous Fries treatment of 3-chloro-*p*-tolyl acetate and *p*-tolyl benzoate gives 3-chloro-2-hydroxy-5-methylbenzophenone and 2-hydroxy-5-methylacetophenone in addition to 3-chloro-2-hydroxy-5-methylacetophenone and 2-hydroxy-5-methylbenzophenone, whereas an intramolecular change should produce only the last two compounds. It appears probable, therefore, that in the Fries change 2 mols. of ester interact. This view is supported by the facts that (1) phenyl acetate reacts with chloroacetyl chloride in presence of aluminium chloride to give some *p*-hydroxyacetophenone chloroacetate, (2) *p*-tolyl acetate, nitrobenzene, and aluminium chloride afford only traces of 2-hydroxy-5-methylacetophenone, whilst (3) addition of thymol in (2) causes the formation of cresol and 4-hydroxy-2-methyl-5-*iso*propylacetophenone.

A similar explanation is given for the conversion of *o*- into *p*-ketones (above). Thus, when 4-hydroxy-3-methylacetophenone and 3-chloro-*p*-cresol are "baked" together, 2-hydroxy-4-methylacetophenone and 3-chloro-2-hydroxy-5-methylacetophenone are formed, whereas on the intramolecular wandering theory only the former should be produced.

E. E. Turner.

Mechanism of the Fries transformation. K. von Auwers and W. Mauss (Annalen, 1928, **464**, 293—311).—The claims of Rosenmund and Schnurr (preceding abstract) in connexion with the general improvement in methods of effecting the Fries transformation require some criticism, for although these authors have considerably improved those methods, some phenol esters, *e.g.*, the acetate and benzoate of 2-hydroxymesitylene, do not undergo the change under the conditions laid down by Rosenmund and Schnurr. Moreover, phenol benzoates and chloroacetates require more drastic treatment than do the corresponding acetates. Thus, phenyl chloroacetate and *m*-tolyl chloroacetate do not undergo the Fries change in 1 day in cold nitrobenzene solution in presence of aluminium chloride, whereas *m*-tolyl acetate and 2-*m*-xylyl acetate, under similar conditions, afford good yields of 2-hydroxy-4-methylacetophenone and 4-hydroxy-3 : 5-dimethylacetophenone, respectively; 4- and 5-*m*-xylyl acetates, the acetate and chloroacetate of 2 : 6-dimethyl-4-ethylphenol, and the *chloroacetate*, b. p. 138°/12 mm., of 3-chloro-*o*-cresol, are to a slight extent hydrolysed, but are otherwise unaffected under these conditions. 2 : 4 : 6-*Trichlorophenyl acetate*, m. p. 49—51°, is unaffected by aluminium chloride in ¼ hr. at 150°, whilst after 4 hrs. at 130—140° in presence of excess of chloride, tar, some trichlorophenol, and a trace of an *o*-hydroxyketone(?) are found present. When heated with aluminium chloride for 1 hr. at 100⟶140°, 3-chloro-*o*-tolyl chloroacetate gives, as main product, 3-*chloro*-4-*hydroxy*-5-*methylphenacyl chloride*, m. p. 98·5—99·5°; whether or not any *o*-displacement of chlorine occurs is uncertain.

Rosenmund and Schnurr's conclusion that the Fries transformation is bimolecular in type, *i.e.*, is a reaction of the Friedel–Crafts type between 2 mols. of a phenol ester, is open to criticism, if for no other reason than that whilst Fries changes lead to *o*- as well as to *p*-compounds, Friedel–Crafts reactions give exclusively the latter. Other evidence, as below, shows the untenability of Rosenmund's view. Meisenheimer and Hanssen (Diss., Tübingen, 1926) have shown that benzoyl chloride and 4-*m*-xylyl methyl ether under Friedel–Crafts conditions give mainly 5-hydroxy-2 : 4-dimethylbenzophenone, *i.e.*, the benzoyl radical goes *meta* to the methoxyl group. Were Rosenmund's contention correct, 4-*m*-xylyl acetate, under Fries conditions, should give 5-hydroxy-2 : 4-dimethylacetophenone, whilst in practice it gives, as the only recognisable product, 2-hydroxy-3 : 5-dimethylacetophenone. Again, when a mixture of the acetate and the methyl ether of 4-*m*-xylenol is warmed with aluminium chloride in nitrobenzene, the ether is unaffected and the acetate gives 2-hydroxy-3 : 5-dimethylacetophenone, *i.e.*, no acetate reacts in the sense to be anticipated from Rosenmund's theory.

The main support for the latter theory is the formation from a mixture of 3-chloro-*p*-tolyl acetate and *p*-tolyl benzoate (Fries conditions) of 3-chloro-2-hydroxy-5-methylbenzophenone and 2-hydroxy-5-methylacetophenone in addition to the normal products, viz., 3-chloro-2-hydroxy-5-methylacetophenone and 2-hydroxy-5-methylbenzophenone. The present authors have obtained the same result, but have also isolated some 3-chloro-*p*-tolyl benzoate. It is shown that exchange of acyl groups frequently occurs when phenol esters of different acids are together submitted to Fries conditions, although this does not necessarily take place with every pair. Thus, a mixture of phenyl acetate and *p*-tolyl chloroacetate gives only 2- and 4-hydroxyacetophenone, and 2-hydroxy-5-methylphenacyl chloride, and, if mild conditions are employed, even the latter is not formed. Similarly, a mixture of *p*-tolyl acetate and 3-chloro-*p*-tolyl benzoate gives only traces of hydroxyketones derived from intermediate reciprocal exchange of acyl radicals. In short, the course of all such reactions is determined by the nature of the substances concerned (the benzoyl and chloroacetyl groups are more firmly attached to oxygen than is the acetyl group). A mixture of 2-*m*-xylyl acetate and *p*-tolyl benzoate gives xylenol and cresol, together with 2-hydroxy-5-methyl-acetophenone and -benzophenone, and 4-hydroxy-3 : 5-dimethylacetophenone. A mixture of the acetate of 2-hydroxymesitylene and *p*-tolyl chloroacetate gives cresol, 2-hydroxymesitylene, the acetate of the latter, and 2-hydroxy-3 : 4 : 5-trimethylacetophenone. The *chloroacetate*, m. p. 77—78°, b. p. 156°/12 mm., of 2 : 6-dimethyl-4-ethylphenol, gives a small quantity of 4-hydroxy-3 : 5-dimethylphenacyl chloride. A mixture of the same chloroacetate with *p*-tolyl acetate ($AlCl_3$; 150°) gives 2-hydroxy-5-methylacetophenone and unchanged chloroacetate, together with a trace of an *o*-hydroxyphenacyl chloride (?).

To determine whether in fact an acyl group attached to the oxygen atom of one phenol can enter the nucleus of another phenol molecule, mixtures of phenol ethers and esters have been heated with aluminium chloride. When 2-*m*-xylyl methyl ether and *p*-tolyl acetate are so taken, the products are xylenol, cresol, 2-hydroxy-5-methyl- and 4-hydroxy-3 : 5-dimethyl-acetophenone. With a mixture of 2-hydroxymesitylene methyl ether and *p*-tolyl chloroacetate, the two free phenols, chloroacetic acid, and unchanged ether are the sole products. Had Rosenmund substitution occurred, ketones derived from the ethers should have been formed.

Other evidence is obtained which shows that reciprocal exchange of acyl groups occurs in some cases under the conditions of a Fries change. 2-Hydroxymesitylene and *p*-tolyl benzoate, or the acetate of the former and *p*-cresol, do not interact in absence of a catalyst at 200°, whilst a mixture of the last two substances, when heated at 150° for ¾ hr. in presence of aluminium chloride, affords only 2-hydroxy-5-methylacetophenone and hydroxymesitylene. On the other hand, when a mixture of 2-hydroxymesitylene and *p*-tolyl benzoate is heated for ¼ hr. at 150° with aluminium chloride, the benzoate of 2-hydroxymesitylene is formed, together with the two free phenols and 2-hydroxy-5-methylbenzophenone, whilst under similar conditions a mixture of the acetate of 2-hydroxymesitylene and *p*-tolyl benzoate affords some of the benzoate of the mesitylenol, together with benzoic acid, 2-hydroxy-5-methylacetophenone, and 2-hydroxy-5-methylbenzophenone. A mixture of the acetate of 2-hydroxymesitylene with 3-chloro-*p*-tolyl benzoate gives free phenols, 3-chloro-2-hydroxy-

5-methyl-acetophenone, the corresponding -benzophenone, and the benzoate of 2-hydroxymesitylene.

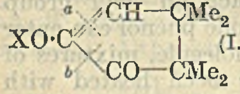
Since reciprocal esterification under Fries conditions would explain Rosenmund's test experiment, it is concluded that the Fries transformation is an intra- and not an inter-molecular change.

E. E. Turner.

Course of the Friedel and Crafts synthesis of ketones with dialkyl [ethers of] resorcinol. F. Mauthner (J. pr. Chem., 1928, [ii], **119**, 311—314).—The "new resacetophenone" obtained by Claus and Huth (A., 1896, i, 227) by the Friedel–Crafts reaction with acetyl chloride and resorcinol diethyl ether was held by Eijkman to be a 4 : 6-diacetoresorcinol; this is confirmed. The action of 2 mols. of acetyl chloride and aluminium chloride on resorcinol dimethyl ether in carbon disulphide yields two products: the first, soluble in alkali, is 4 : 6-diacetoresorcinol monomethyl ether (Eijkman, Bergema, and Henrard, A., 1905, i, 360), and the second, insoluble in alkali, the corresponding dimethyl ether. Free resorcinol gives 4 : 6-diacetoresorcinol and (?) its dimethyl ether; resorcinol diethyl ether yields 4 : 6-diacetoresorcinol monoethyl ether.

E. W. Wignall.

Possibility of ring–chain valency tautomerism, and of a type of mobile hydrogen tautomerism analogous to the Wagner–Meerwein rearrangement. III. Orientation of some cyclic derivatives of phorone. C. K. Ingold and C. W. Shoppee (J.C.S., 1928, 1868—1873).—The structure (I), previously assigned (this vol., 414) to the acetyl derivative (X=Ac) of hydroxyphorone (5-hydroxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone), is confirmed, since the dihydro-derivative yields an *oxime*, m. p. 93° (*hydrochloride*, m. p. 136—137°), which is reduced by sodium amalgam to 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. The formation of an oxime from 5-benzoyloxyphorone with extrusion of the benzoyl grouping as previously stated (*loc. cit.*) leaves doubtful the position in which the oximino-grouping has become attached to the ring. It is now shown that reduction of the oxime by sodium amalgam followed by phosphorus and hydriodic acid yields 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine; moreover, 5-benzoyloxyphorone is reduced by hydrogen and palladised barium sulphate to 5-benzoyloxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanolone. The original benzoyloxy-compound must therefore have the structure (I) (X=Bz), and the oximino-group must enter the molecule in a position other than that from which the benzoyl group is expelled. 5-*p*-Bromobenzyloxyphorone is only very slightly affected by palladised barium sulphate and hydrogen, yielding a *compound*, m. p. 26—27°. Reduction of 5-*p*-bromobenzyloxy-2 : 2 : 3 : 3-Δ^4-*cyclo*pentenoneacetoxime with sodium amalgam and acetic acid yields 5-hydroxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine, isolated as the picrate, and further reduction with phosphorus and hydriodic acid affords 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. It is shown that hydroxylamine can hydrolyse phenyl benzoate and 5-benzoyloxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone, and that the methyl group of 5-methoxyphorone is removed by treatment with hydroxylamine, yielding the dioxime of 3 : 3 : 4 : 4-tetramethyl*cyclo*pentan-1 : 2-dione. The normal mode of fission of hydroxyphorone or its derivatives by oxidation with potassium ferricyanide is at (*a*) (I), whilst fission with hydrogen peroxide occurs preferentially at (*b*) (I). Thus with potassium ferricyanide, 5-benzoyloxyphorone yields the lactonic acid of γγ-dihydroxy-ααββ-tetramethylglutaric acid, whilst 5-acetoxyphorone and 5-hydroxyphorone yield tetramethylsuccinic acid. Benzoyloxyphorone and hydrogen peroxide yield ααββ-tetramethylglutaric acid.



(I.)

M. Clark.

Relative reactivity of methylene groups in 1 : 3-diketones. A. B. E. Lovett and E. Roberts (J.C.S., 1928, 1975—1979).—ω-Phenylacetylacetophenone (I) condenses with salicylaldehyde in absolute alcohol solution in presence of piperidine, giving *o-hydroxybenzylidenephenylacetylacetophenone*, $OH{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CO{\cdot}CH_2{\cdot}CO_2Ph$, m. p. 171—174°. The constitution of this substance is fixed, since it is readily converted into acetophenone and 3-phenylcoumarin. The following substituted 3-phenylcoumarins in small yield are produced when the appropriate substituted salicylaldehydes are condensed with (I), but in these cases no intermediate product can be isolated: 6-*methyl*-, m. p. 146—147·5°; 6-*chloro*-, m. p. 199°; 6-*bromo*-, m. p. 189—191°; 6-*nitro*-, m. p. 251—253°; 8-*nitro*-, m. p. 236—239°; 6 : 8-*dichloro*-, m. p. 193—194·5°; 6 : 8-*dibromo*-, m. p. 186—187·5°; 6-*bromo*-8-*nitro*-, m. p. 228—230°; and 8-*nitro*-6-*methyl*-3-*phenylcoumarins*, m. p. 180—182°. 3 : 5-*Dinitrosalicylaldehyde* (II), m. p. 58—60°, is obtained by further nitration of the mixture of 3- and 5-nitrosalicylaldehydes produced by mononitration of salicylaldehyde; on oxidation it gives 3 : 5-dinitrosalicylic acid. 5-*Chloro*-3(?)-*nitrosalicylaldehyde* (III), m. p. 105—107°, is produced by nitration of 5-chlorosalicylaldehyde in glacial acetic acid. Its constitution is inferred from that of the analogous 5-bromo-3-nitrosalicylaldehyde. Aldehydes (II) and (III) fail to give substituted 3-phenylcoumarins with (I). Like 5-bromo-3-nitrosalicylaldehyde, from which only a trace of the corresponding coumarin is obtained, they react with piperidine to give stable piperidides of undetermined constitution. 6 : 8-*Dinitro*- and 6-*chloro* 8(?)-*nitro*-3-*phenylcoumarin*, synthesised by the Perkin reaction, have m. p. 244—246° and 212—214°. Ethyl phenylacetate and salicylaldehyde give some 3-phenylcoumarin when heated in presence of piperidine. 2-Hydroxy-α-naphthaldehyde and (I) react in alcoholic solution in presence of piperidine, giving a deep red *compound*, $C_{27}H_{18}O_2$, m. p. 155—156·5°. ω-Propionylacetophenone, b. p. 149°/17 mm., 151°/19 mm. (*copper* salt, m. p. 151—152°; p-*nitrophenylhydrazone*, m. p. 67—68°; *anil*, m. p. 48—49°), butyrylacetophenone, and propionylacetone yield resin-like products when treated with salicylaldehyde. It is deduced that the methylene group in (I) more reactive for condensation with aldehydes, is that adjacent to the phenyl group.

M. Clark.

Syntheses of β-4-hydroxy-3-methoxystyryl *n*-propyl and *n*-amyl ketones. S. Tsurumi, S. Murakoshi, and R. Yamasaki (Sci. Rep. Tôhoku Imp. Univ., 1928, **17**, 703—705).—The condensation of vanillin with methyl *n*-propyl and *n*-amyl ketones to yield β-4-hydroxy-3-methoxystyryl *n*-propyl and *n*-amyl ketones (cf. Nomura and Hotta, A., 1925, i, 1156; Murai, *ibid.*, 1157) takes place readily on boiling for 6 hrs. with aqueous-alcoholic potassium hydroxide. R. K. CALLOW.

Syntheses of β-4-hydroxy-3-methoxyphenylethyl *n*-pentenyl and *n*-hexenyl ketones. H. NOMURA and S. EL CHOI (Sci. Rep. Tôhoku Imp. Univ., 1928, **17**, 707—710; cf. Nomura and Tsurumi, A. 1927, 1078).—Condensation of zingerone (β-4-hydroxy-3-methoxyphenylethyl methyl ketone) with *n*-butaldehyde and *n*-valeraldehyde in presence of aqueous potassium hydroxide yielded, respectively, β-4-*hydroxy-3-methoxyphenylethyl* n-*pentenyl ketone*, b. p. 198·5—200°/4·5 mm., and the n-*hexenyl ketone*, b. p. 203—206·5°/6 mm. The constitutions were confirmed by reduction with hydrogen in presence of platinum-black to the known saturated ketones (Murai, A., 1925, i, 1157; Nomura and Tsurumi, *loc. cit.*).

R. K. CALLOW.

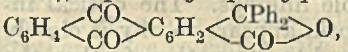
Chemical constitution and pungency. E. MARUI (Sci. Rep. Tôhoku Imp. Univ., 1928, **17**, 695—702).—In view of the reported pungency of β-*o*-hydroxy- and β-2-hydroxy-3-methoxy-phenylethyl methyl ketones the author prepared other *o*-hydroxy-derivatives of this type. *o*-Hydroxystyryl ethyl ketone, m. p. 116—118° (cf. Auwers and Voss, A., 1910, i, 70), yields, on reduction by sodium amalgam, β-o-*hydroxyphenylethyl ethyl ketone*, m. p. 72° (I). *o*-Hydroxystyryl phenyl ketone (cf. Harries and Busse, A., 1896, i, 301) is reduced by hydrogen in the presence of platinum-black to β-*o*-hydroxyphenylethyl phenyl ketone, m. p. 91° (II) (cf. Borsche and Geyer, A., 1914, i, 711). β-*o*-Hydroxyphenylethyl methyl ketone is reduced by amalgamated zinc and hydrochloric acid to δ-o-*hydroxyphenylbutane*, b. p. 101—102°/11 mm. (III). The *sodium* (+H_2O), *potassium* (+H_2O), and *calcium* salts of hydro-*o*-coumaric acid (β-*o*-hydroxyphenylpropionic acid) (IV) (cf. Tiemann and Herzfeld, A., 1877, i, 708) were prepared. Compounds (I) and (III) are pungent. (II) is first sweet and then pungent. The salts of (IV) are pungent in proportion to their solubility. The anhydride, ethyl ester, and amide, m. p. 92° (lit. 70°), are all pungent.

R. K. CALLOW.

Reduction of quinones by means of phenylhydrazine. A. GIACALONE (Gazzetta, 1928, **58**, 409—411).—Phenylhydrazine reduces quinones to quinols; with benzoquinone the reaction is so violent that benzene must be used as a diluent; thymoquinone is reduced in benzene, but with naphthaquinone [which with phenylhydrazine hydrochloride in acetic acid gives benzeneazo-α-naphthol (Zincke and Bindewald, A., 1885, 391)] reduction to the quinol occurs only in absence of solvent. Anthraquinone is not reduced. E. W. WIGNALL.

Reaction of malononitrile with α-naphthaquinone. W. KESTING (Z. angew. Chem., 1928, **41**, 745—748; cf. this vol., 606).—The intense blue coloration developed when neutral aqueous solutions (p_H greater than 2·5) of malononitrile and α-naphthaquinone are mixed is due to formation of β-*imino*-β-1 : 4-*naphthaquinonylpropionitrile*, $C_{10}H_5O_2\cdot C(NH)\cdot CH_2\cdot CN$, m. p. above 250° (decomp.; *silver* salt). The blue *ammonium* salt, obtained by passing ammonia into an ethereal solution of the components, dyes wool in bright violet shades, becoming black on exposure to light. The red *hydrochloride*, precipitated by hydrochloric acid from a solution of the ammonium salt, loses hydrogen chloride on exposure to moist air, giving the imino-nitrile, this being the only way in which the latter could be prepared in solid form. C. HOLLINS.

Course of the Friedel–Crafts reaction with anthraquinone-1 : 2-dicarboxylic anhydride. G. MACHEK and A. GRAT (Monatsh., 1928, **50**, 6—9).—The condensation of anthraquinone-1 : 2-dicarboxylic anhydride with benzene in presence of aluminium chloride gives, in place of the expected 1 : 2 : 3 : 4-diphthaloylbenzene (cf. Fairbourne, J.C.S., 1921, **119**, 1580), a *phthaloyldiphenylphthalide*,


$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{CPh_2}{CO}{>}O$, m. p. 180—182°, and the corresponding hydroxy-acid, $C_{28}H_{18}O_5$, m. p. 143—146°. C. HOLLINS.

Stereochemistry of aromatic compounds. VI. An optically active vat dye without an asymmetric carbon atom; *d*- and *l*-1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid. R. KUHN and O. ALBRECHT (Annalen, 1928, **464**, 91—100).—2 : 2′-Dimethyl-1 : 1′-dianthraquinonyl has been prepared by Scholl's method (A., 1924, i, 60). The intermediately used 1-iodo-2-methylanthraquinone has m. p. 172·5—173·5° (corr.), not 169—169·5° as given by Scholl. Oxidation of the dimethyl derivative with chromic anhydride in acetic anhydride and glacial acetic acid affords 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid in higher yield than that given by Scholl's method. The acid cannot be resolved through its brucine or morphine salts, but addition of light petroleum to a concentrated chloroform solution of the quinine salt effects partial resolution (see original for details). *Quinine* l-1 : 1′-*dianthraquinonyl*-2 : 2′-*dicarboxylate*, having $[\alpha]_D^{18}$ −110·7° (not optically pure), leads to the optically impure l-*acid*, $[\alpha]_D^{18}$ −237° in 0·1*N*-sodium hydroxide. The *quinine* salt of the *d*-acid, obtained optically pure, has m. p. 249—250°, $[\alpha]_D^{18}$ +369° in pyridine, and leads to the optically pure d-*acid* (m. p. phenomena indefinite, as with *l*-acid), $[\alpha]_D^{19}$ +346° in 0·1*N*-sodium hydroxide (rotatory dispersion measured). The *d*-acid does not undergo racemisation in 0·1*N*-sodium hydroxide during 6½ hrs. at 140—160°, nor in acetic anhydride during 7½ hrs. at 100°, but some racemisation occurs in acetic anhydride after 3½ hrs. at the b. p. of the solution. Conversion of the *d*-acid into a vat, using alkaline hyposulphite, and subsequent recovery of acid by oxidation appears to be without great effect on the activity. Some inconclusive experiments on dyeing viscose, hair, and wool have been made.

The non-co-planar configuration of the dianthraquinonyl molecule is demonstrated by the above resolution. E. E. TURNER.

Constitution of carotin. L. ZECHMEISTER and L. VON CHOLNOKY (Ber., 1928, **61**, [*B*], 1534—1539).—Catalytic hydrogenation of carotin in *cyclo*hexane in the presence of platinum shows that its double linkings are divisible into two groups. At least two and probably three of them are distinguished by not being causative of colour; they become hydrogenated towards the end of the reaction after the double linkings of the second type have become almost completely saturated. The colour of carotin is due to a series of double linkings which readily absorb hydrogen. As long as hydrogenation mainly affects the latter type, the diminution in the intensity of the colour of the solution is proportional to the consumption of hydrogen. The colour appears to be lost completely after addition of 8 mols. of the gas. Partly hydrogenated solutions of carotin all exhibit the typical carotin spectrum and hence contain a mixture of unchanged material and decolorised products; coloured intermediate compounds do not appear to be formed. Carotin therefore appears to contain eight olefinic linkings conjugated with one another and three further double linkings. The optical inactivity of perhydrocarotin appears to ally it closely to perhydro-ψ-crocetin and to strengthen further the analogy between the safran dyes and the carotin group. Perhydrocarotin, $C_{40}H_{78}$, conveniently prepared by catalytic hydrogenation of carotin in chloroform in the presence of platinum, has normal mol. wt. in freezing benzene, indicating a C_{40} formula for carotin, which is supported by direct determinations of its mol. wt. in freezing benzene and camphor. H. WREN.

Crystalline carotin-like substances from meadow ranunculus and rose "hips." H. H. ESCHER (Helv. Chim. Acta, 1928, **11**, 752—754).—Details are given for the extraction of xanthophyll from the flowers of *Ranunculus Steveni*, Andrz., and of lycopin from rose "hips" (cf. Willstätter and Escher, A., 1910, i, 330; 1912, i, 125). H. BURTON.

Plant colouring matters. VII. Lycopin. P. KARRER and R. WIDMER (Helv. Chim. Acta, 1928, **11**, 751—752).—Catalytic reduction of lycopin (Willstätter and Escher, A., 1910, i, 330) gives *perhydrolycopin*, $C_{40}H_{82}$, b. p. 238—240°/0·03 mm., thus demonstrating its aliphatic nature and its similarity to carotin and bixin (this vol., 869). H. BURTON.

Gossypol. IV. *apo*Gossypol. E. P. CLARK (J. Biol. Chem., 1928, **78**, 159—166; cf. this vol., 208, 426).—By heating gossypol with 40% sodium hydroxide at 100° and acidifying there was obtained apo*gossypol*, $C_{28}H_{30}O_6$ (*hexa-acetate*, m. p. 291°; *hexamethyl ether*, m. p. 259°); the mother-liquor yielded 2 mols. of formic acid which must have arisen from the two carbonyl groups of gossypol; as in gossypol hexa-acetate, two of the acetyl groups of *apo*gossypol hexa-acetate are more resistant to hydrolysis than the remaining four. *apo*Gossypol is considerably less toxic than gossypol, and causes acute effects only. C. R. HARINGTON.

Salep-mannan. H. PRINGSHEIM and G. LISS (Annalen, 1928, **460**, 32—42).—Salep-mannan is converted by acetic anhydride in presence of glacial acetic acid and pyridine, under certain prescribed conditions, into the *triacetate*, $[\alpha]_D^{19}$ −28·9°. This has M in acetic acid (f. p.) 293—717 and in nitrobenzene (f. p.) 518—1355. The degradation of the triacetate by heat in presence of naphthalene has been examined. E. E. TURNER.

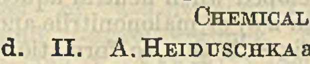
Relation of lichosan to lichenin. II. H. PRINGSHEIM and H. BRAUN (Annalen, 1928, **460**, 42—56).—The viscosities of a number of lichenin solutions have been measured. The fermentative degradation of lichosan has been studied under various conditions. The different effects of ageing on aqueous solutions of lichosan and of lichenin is noted. The *product*, $C_6H_9O_4{\cdot}O{\cdot}PO_3H$, has been obtained by treating lichosan with phosphoryl chloride in presence of pyridine at −15°. E. E. TURNER.

Hypothetical combined pentose and so-called free pentose [in apples]; composition of pectin. R. B. MCKINNIS (J. Amer. Chem. Soc., 1928, **50**, 1911—1915).—A 95% alcoholic extract of apple pulp yields no furfuraldehyde when distilled with 12% hydrochloric acid. Free pentose is therefore absent, or present only in small amount. Determinations of the galacturonic acid content of the pulp from the amount of carbon dioxide liberated on hydrolysis, and of the yield of furfuraldehyde from Ehrlich's digalacturonic acid (A., 1917, i, 321) by distillation with hydrochloric acid, indicate that the furfuraldehyde formed when the whole apple pulp is distilled with acid is entirely accounted for by the galacturonic acid present. Pentoses, either free or combined, do not, therefore, occur in apples or in apple pectin (cf. Nanji, Paton, and Ling, J.S.C.I., 1925, **44**, 253T), although arabinose is probably an intermediate stage in the conversion of galacturonic acid into furfuraldehyde. H. E. F. NOTTON.

Acid constituents of sandarac resin. A. ROLLETT (Monatsh., 1928, **50**, 1—5).—At least three acids are probably present in sandarac resin. Sandaracic acid (*methyl* ester, m. p. 159°) and sandaricinolic acid, m. p. 199° [acetic anhydride isomerisation product (?), m. p. 223°]; are amorphous and labile (Wolf, Diss., Bern, 1906; Henry, Diss., London, 1901). A third acid, $C_{20}H_{30}O_3$, m. p. 263°, for which the old name "callitropic acid" is adopted, is now obtained pure and crystalline. C. HOLLINS.

Betulin. I. K. A. VESTERBERG and R. VESTERBERG. **II.** R. VESTERBERG (Arkiv Kemi, Min., Geol., 1928, **9**, No. 27, 1—17; No. 45, 1—11).—An amplified account of work already published (A., 1923, i, 590; 1927, 882). Dihydrobetulin diformate has m. p. 268°.

Oxidation of santonin. II. Rotatory power of some oxidation products of santonin. S. S. MEDVEDEV and E. N. ALEKSEEVA (Trans. Karpov Inst. Chem., 1926, No. 5, 57—61).—Santoninic, santonic, and santenonic acid have $[\alpha]_D$ −26·5°, −70·0°, and −125·5°, respectively, supporting the view that these acids have similar configurations. Santenonic acid, when heated in a vacuum, loses 2 mols. of water, yielding an unsaturated lactone, santonene, $C_{15}H_{16}O_3$, $[\alpha]_D$ −280·9° (acetyl derivative, $[\alpha]_D$ −1507° in alcohol, −1500° in chloroform, the high value indicating the formula



$$\begin{array}{l}\mathrm{CH_2{\cdot}CMe{:}C{\cdot}CH_2{\cdot}C{\cdot}O{\cdot}CO}\\ \mathrm{CO{-}CMe{:}C{\cdot}CH_2{\cdot}C{-}CMeAc}\end{array}$$

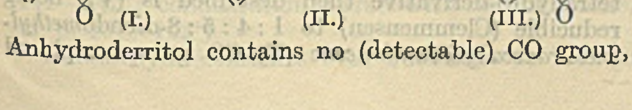
). CHEMICAL ABSTRACTS.

Cacao-red. II. A. HEIDUSCHKA and B. BIENERT (J. pr. Chem., 1928, [ii], **119**, 199—208; cf. B., 1928, 118).—Distillation of cacao-red with large excess of zinc dust in a stream of carbon dioxide gives mainly mesitylene. By acetylation of cacao-red in pyridine with acetyl chloride in chloroform below 0° between 8 and 9 acetyl groups are taken up, and a *compound*, decomp. 210—215°, is formed. Benzoylation gives similar results (*product*, decomp. 219—220°), but with methyl sulphate there are obtained a *heptamethyl ether*, decomp. 213—216°, and a mixture, decomp. 215°, of *tri-* and *penta-methyl ethers*. An impure phenylhydrazone of cacao-red is described, and the constitution further discussed. C. Hollins.

Rotenone, the physiologically active constituent of *Derris elliptica*. A. Butenandt [and, in part, O. Linsert and D. Botschwar] (Annalen, 1928, **464**, 253—277).—Rotenone may be distilled in a high vacuum (b. p. 210—220°/0·5 mm.). Its hydrochloride has m. p. 194°, not 188° as given by Takei (this vol., 765). The presence of only one ethylenic linking in rotenone (Kariyone and co-workers, A., 1923, i, 477; 1924, i, 251) is confirmed, hydrogenation in presence of palladised barium sulphate giving dihydrorotenone, m. p. 214—216°, which with nitrous acid affords a *diketone*, m. p. 317° (decomp.). The carbonyl group in rotenone is also reduced if hydrogenation is carried out in presence of platinum, the resulting *dihydrodeoxyrotenone*, $C_{23}H_{26}O_5$, m. p. 168°, b. p. 220—230°/vac., having, however, little reactivity. Hydrogenation of rotenone in alcoholic ammonia in presence of platinum gives a *substance*, $C_{23}H_{26}O_6$, m. p. 206°.

In weakly acid solution rotenone gives an oxime (m. p. 249°; Takei gives 239°, Kariyone, 245°) and a hydrazone distinct from the iso*oxime*, m. p. 230°, and iso*hydrazone*, m. p. 229°, formed in presence of alkali (iso*phenylhydrazone* has m. p. 203°). The *iso*-derivatives may be formed as a result of scission of an oxide ring by the alkali, ring-closure subsequently occurring in a different position.

Rotenone contains the $\cdot CO\cdot CH_2\cdot$ grouping, since ethyl nitrite and acetic and hydrochloric acids afford a *diketone*, $C_{23}H_{20}O_7$, m. p. 298—300° (decomp.), $[\alpha]_D^{19}$ −3·5° in chloroform, possibly identical with Takei's rotenonone (A., 1925, i, 761). Treatment of rotenone with zinc dust and alcoholic potassium hydroxide produces *derritol*, $C_{21}H_{22}O_6$, m. p. 161° (a phenolic compound containing CO and 2OMe and giving, when distilled at 220—225°/0·06 mm., *anhydroderritol*, $C_{21}H_{20}O_5$, m. p. 157°, not reconvertible into derritol), together with *rotenol*, $C_{23}H_{24}O_6$, m. p. 115—120°, b. p. 200—210°/vac., which may be the secondary alcohol corresponding with the ketone, rotenone. Rotenol is hydrogenated in presence of platinum, giving *dihydrorotenol*, $C_{23}H_{26}O_6$, m. p. 131°, also obtained by the reduction of dihydrorotenone with zinc dust and alkali. Both rotenol and dihydrorotenol behave towards alkali as lactones. Possibly the annexed scheme represents the inter-relationship of rotenone (I), derritol (II), and anhydroderritol (II):



(I.) (II.) (III.)

Anhydroderritol contains no (detectable) CO group, but contains an ethylenic linking and a hydroxyl group, since it affords an *acetyl* derivative, m. p. 146°, which is hydrogenated in acetic acid in presence of platinum, giving a *dihydro*-derivative, m. p. 131°.

Treatment of rotenone with alkali affords tubaic acid, m. p. 129°, b. p. 130—140°/vac. (cf. Kariyone) (*acetate*, m. p. 133°; *methyl* ester, m. p. 48°, b. p. 120°/vac.), which on reduction gives *dihydrotubaic acid*, m. p. 166°. Since the latter is also obtainable from dihydrorotenone by a similar process, the alkali scission of rotenone involves the carbonyl group and not the ethylenic linking. Tubaic acid contains a hydroxyl group which, although acetylatable, is not methylated by diazomethane, so that the hydroxy-group may have two substituents *ortho* to it. Tubaic acid contains one methoxyl-free benzene ring, and to this benzene ring, in rotenone, at least one oxide ring must be attached (production of phenolic hydroxyl in presence of alkali). Moreover, the two benzene rings in rotenone are separated by a carbon chain. Further, since rotenone with alkali affords a phenolcarboxylic acid, rotenone and dihydrorotenone must contain a β-keto-acid lactone or a β-diketone grouping.

Oxidation of rotenone with chromic anhydride in acetic acid (Takei) gives rotenonone, whilst if the mother-liquor is freed from acid and then treated with diazomethane, a mixture of esters results, from which, by hydrolysis, tubaic acid is obtainable. Rotenonone forms a *dihydrazone*(?), m. p. 242°, and is hydrogenated in acetic acid (platinum) to *perhydrorotenonone*, $C_{23}H_{26}O_6$, m. p. 265—267° (decomp.) (*acetyl* derivative, m. p. 245°). Treatment of rotenonone (cf. Takei) with alcoholic potassium hydroxide at 100° produces a *hydroxy-acid*, $C_{23}H_{22}O_8$, m. p. 250° (*methyl* ester, m. p. 146—147°), possibly formed by a benzilic acid change from the diketone.

Rotenone is readily dehydrogenated to *dehydrorotenone*, m. p. 218°, b. p. 240—250°/vac., this change being effected by potassium permanganate in acetone containing alcoholic potassium hydroxide, by iodine and alcoholic potassium acetate, by potassium ferricyanide in aqueous methyl-alcoholic potassium hydroxide, by perbenzoic acid, or by alcoholic ammonia at 100°. Dehydrorotenone is possibly identical with the "crystalline yellow material" described by other workers as having m. p. ranging from 214° to 233°. It is converted by boiling alcoholic potassium hydroxide into a *hydroxyketo-acid*, $C_{23}H_{24}O_8$, m. p. 152°, which contains a methoxyl group and, when hydrogenated (acetic acid, platinum), passes into an *acid*, $C_{23}H_{26}O_8$, m. p. 168°. It therefore contains an ethylenic linking; it also contains a carbonyl group, for it gives an *oxime*, m. p. 200°.

The constitution of rotenone remains unsettled, but the author regards rotenone as possibly being not very different in general type from bergapten and xanthotoxin. E. E. Turner.

Catalytic action. XXII. Catalytic action of reduced copper on unsaturated hydrocarbons. S. Komatsu and M. Kurata (Mem. Coll. Sci. Kyōtō, 1928, **11**, [*A*], 164—169; cf. A., 1925, i, 942).—When menthene is passed over reduced copper at 290—300°, menthane and *p*-cymene are produced. *d*-Limonene is converted completely into cymene at 280—300°, but at 200° menthane, dipentene, and carvomenthene are formed also. Similar treatment of *d*-β-phellandrene at 300° gives cymene (82%) and menthane.

H. BURTON.

Transformation of aliphatic terpenes into monocyclic terpenes. Synthesis of menthol. R. HORIUCHI (Mem. Coll. Sci. Kyōtō, 1928, **11**, [*A*], 171—197).—*d*-Citronellal is converted by 5% sulphuric acid at 25—30° into *iso*pulegol (7%), menthoglycol (75%), and an *ether* (3%), $C_{20}H_{30}O_2$, b. p. 191·5°/16 mm., d_4^{20} 0·9341, n_D^{20} 1·476, $[\alpha]_D$ −5° 30′, which is reduced catalytically to a *compound*, $C_{20}H_{38}O_2$, d_4^{20} 0·9155, n_D^{20} 1·4635, $[\alpha]_D$ −2° 52′ (cf. Barbier and Leser, A., 1897, i, 537). When 20% sulphuric acid is used, the corresponding percentage yields are 9, 39, and 21. The action of 50% sulphuric acid on citronellal is to form a *terpene* (I), $C_{10}H_{16}$, d_4^{20} 0·8535, n_D^{25} 1·4875, together with the above ether. Potassium hydrogen sulphate and citronellal react at 140°, yielding *iso*pulegol and di*iso*pulegyl ether, (II), $C_{20}H_{34}O$, b. p. 185°/12·5 mm., d_4^{20} 0·9120, n_D^{20} 1·4835, $[\alpha]_D$ +12° 15′, reduced catalytically to the saturated *ether*, d_4^{20} 0·8932, n_D^{20} 1·4678, $[\alpha]_D$ +6° 1′. Acetic acid, acetic anhydride, or acetic anhydride and sodium acetate convert citronellal at 150° into *iso*pulegyl acetate, although with the last reagents some citronellal mono- and di-enol-acetates are produced also. When *iso*pulegol is treated with 20% sulphuric acid, menthoglycol is formed, but with 50% acid a terpene similar to (I) is obtained. Menthoglycol is unaffected by 20% sulphuric acid, with 50% acid a partial transformation into (I) occurs, and with potassium hydrogen sulphate (I) and (II) are formed.

Citral is converted by 20% sulphuric acid into a *hydrocarbon*, $C_{10}H_{14}$, b. p. 183—186°, d_4^{20} 0·8886, n_D^{20} 1·5092, together with products which are decomposed by heat, whilst with 50% acid *p*-cymene is the main product. Potassium hydrogen sulphate and citral at 140° give *p*-cymene and a *hydrocarbon*, $C_{20}H_{28}$, b. p. 190—194°/14 mm., d_4^{20} 0·9244, n_D^{20} 1·528, whilst acetic acid at 150° yields *p*-cymene.

When *iso*pulegol is reduced by hydrogen in presence of platinum-black and glacial acetic acid *l*-menthol is obtained.

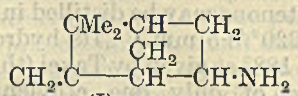
H. BURTON.

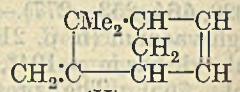
Production of inactive menthol (racemate of natural menthol). RHEINISCHE KAMPFER FABR. —See B., 1928, 547.

[Natural occurrence of inactive camphor.] Phenyl- and α-naphthyl-carbamylhydrazones [-semicarbazones] of inactive camphor. V. MORANI (Gazzetta, 1928, 58, 404—409).—The essential oil of *Salvia officinale* contains *dl*-camphor. The oxime and semicarbazone of this are prepared and have the normal m. p., 176·5—177° and 236—238°; but when the semicarbazone is heated with aniline, dl-*camphor phenylsemicarbazone* is obtained, m. p. 171·5—172·5°. Synthetic *dl*-camphor gives a product of identical m. p., different from that of the *d*-camphor derivative, viz., 153—154° (Borsche, A., 1902, i, 186; Borsche and Merkwitz, A., 1904, i, 945). *dl*-Camphor can thus be characterised; there is also a difference in m. p. between d-*camphor* and dl-*camphor α-naphthylsemicarbazones*, m. p. 172·5° and 179—180° (from either natural or synthetic *dl*-camphor), respectively. These are prepared by heating with α-naphthylamine in quinoline, which is removed by dilute sulphuric acid; *acetophenone α-naphthylsemicarbazone* has m. p. 208°.

E. W. WIGNALL.

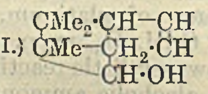
***iso*Camphodiene, a new dicyclic, doubly unsaturated hydrocarbon, and bornylenol, the product of its hydration.** S. NAMETKIN and A. ZABRODIN (Ber., 1928, 61, [*B*], 1491—1494).—α-Aminocamphene (I) is converted by potassium hydroxide and methyl iodide into the corresponding *quaternary iodide*, transformed by silver oxide into the ammonium base which, when distilled, affords iso*camphodiene* (II), m. p. 41·5—42°, b. p. 149—150°/763 mm., closely resembling camphene.

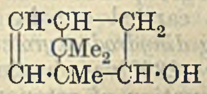

(I).


(II).

The hydrocarbon is transformed by glacial acetic and sulphuric acids into *bornylenyl acetate*, b. p. 106—107°/18 mm., d^{20} 1·0019, n^{20} 1·4662, hydrolysed by potassium hydroxide to *bornylenol* (III) or (IV), m. p. 60—61°.

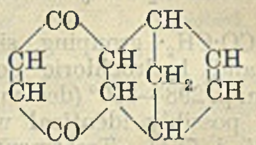
(III.)

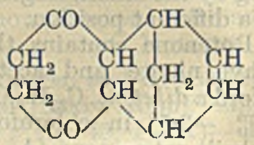



(IV.)

H. WREN.

Syntheses in the hydroaromatic series. I. Additions of di-" en "-hydrocarbons. O. DIELS and K. ALDER (Annalen, 1928, 460, 98—122).—The compound obtained by Albrecht (A., 1906, i, 674) by the combination of a molecule each of cyclo*pentadiene* and *p*-benzoquinone is shown to be (I), as already suggested by Diels, Blom, and Koll (A., 1925, i, 976). The dihydro-derivative, m. p. 34—35°, obtained by Albrecht, which must be (II), is hydrogenated, in alcohol, in presence of colloidal palladium, to 1 : 4-endo*methylene*-5 : 8-*diketodecahydronaphthalene* (III), m. p. 56—57° [*dioxime*, m. p. 217—218° (decomp.)], and this, by Clemmensen's method, is reducible to 1 : 4-endo*methylenedecahydronaphthalene*, b. p. 84—85°/15 mm. or 91°/22 mm.


(I.)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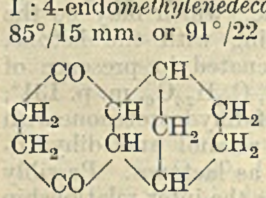
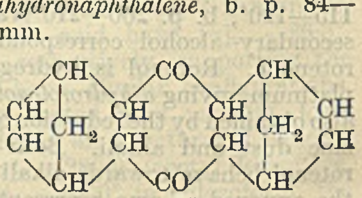
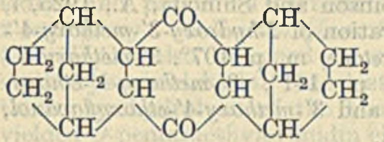
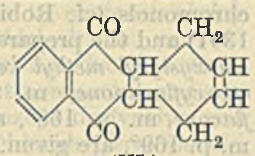

(III.)


(IV.)

The compound obtained by Albrecht from 1 mol. of *p*-benzoquinone and 2 mols. of cyclo*pentadiene* is (IV), as previously suggested (1925, *loc. cit.*), and the tetrahydro-derivative then described is (V), being reducible (Clemmensen) to 1 : 4 : 5 : 8-*diendo**methylenetetradecahydroanthracene* (V, CO groups replaced by CH_2), b. p. 157—159°/16 mm. This, when heated with selenium at 360—380°, affords 1 : 4 : 5 : 8-*di-*

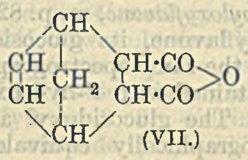

(V.)

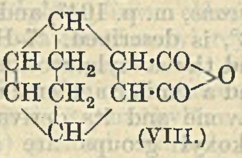

(VI.)

endo*methylene*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene*, m. p. 157°.

Butadiene combines at 100° with α-naphthaquinone to give Δ^2-*tetrahydroanthraquinone* (VI), m. p. 102—103°, converted by chromic anhydride in acetic acid into anthraquinone.

Maleic anhydride and *cyclo*pentadiene combine in cold benzene solution to give cis-3 : 6-endo*methylene*-Δ^4-*tetrahydrophthalic anhydride* (VII), m. p. 164—165°,

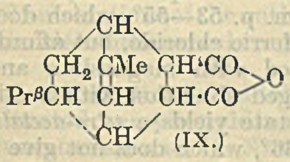

(VII.)

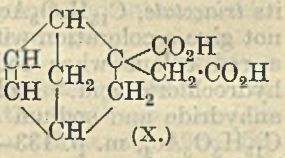

(VIII.)

converted by boiling water into the corresponding *acid*, m. p. 177—179°. Reduction of the *sodium* salt of the latter (hydrogen and palladium) gives cis-3 : 6-endo*methylenehexahydrophthalic* (cis-3 : 6-endo*methylene*cyclo*hexane*-1 : 2-*dicarboxylic*) *acid*, m. p. 160—161° (*anhydride*, m. p. 167—168°). The *trans*-acid, m. p. 194—195°, results when the *cis*-acid is heated with concentrated hydrochloric acid at 180—190°.

Butadiene combines with maleic anhydride to give cis-Δ^4-*tetrahydrophthalic anhydride*, m. p. 103—104°; the corresponding *acid*, m. p. 166°, is catalytically reducible to *cis*-hexahydrophthalic acid.

*cyclo*Hexadiene and maleic anhydride combine in cold benzene solution to give endo*dimethylene*-Δ^4-*tetrahydrophthalic anhydride* (VIII), m. p. 147°, not affected by boiling water. α-Phellandrene and maleic anhydride similarly afford the *anhydride* (IX), m. p. 126—127°.


(IX.)


(X.)

Citraconic anhydride and *cyclo*pentadiene afford 1-*methyl*-3 : 6-endo*methylene*-Δ^4-*tetrahydrophthalic anhydride*, m. p. 138°, whilst itaconic anhydride similarly produces the *anhydride*, m. p. 53—54°, of 2 : 5-endo*methylene*-Δ^3-cyclo*hexenylidenesuccinic acid* (X), m. p. 150—151°. Acrylic acid and *cyclo*pentadiene give 2 : 5-endo*methylene*-Δ^3-*tetrahydrobenzoic acid*, b. p. 132—134°/22 mm., reducible to the corresponding *hexahydro-acid*, m. p. 62—63°. Similarly, acraldehyde gives 2 : 5-endo*methylene*-Δ^3-*tetrahydrobenzaldehyde*, b. p. 70—72°/20 mm. (*semicarbazone*, m. p. 162°; condensation *product* with cylco*hexanone*, m. p. 105°), reduced catalytically to the corresponding *hexahydroaldehyde*, b. p. 75—76°/25 mm. (*semicarbazone*, m. p. 141—142°; condensation *product* with *cyclo*hexanone, m. p. 101—102°).

Acraldehyde combines with butadiene at 100° to give Δ^3-*tetrahydrobenzaldehyde*, b. p. 51—52°/13 mm. (together with a glassy polymeride) (*semicarbazone*, m. p. 153—154°, reducible to hexahydrobenzaldehyde semicarbazone). E. E. Turner.

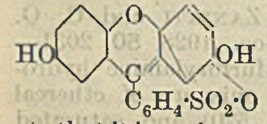
Esters of tetrahydro-α-furfuryl alcohol. J. E. Zanetti (J. Amer. Chem. Soc., 1928, **50**, 1821—1822).—The following esters, which, unlike the corresponding derivatives of α-furfuryl alcohol (A., 1925, i, 567, 953), are stable towards aërial oxidation, may be prepared by any of the usual methods : *tetrahydro-α-furfuryl acetate*, b. p. 194—195°/753 mm., d_0^{20} 1·061; *propionate*, b. p. 85—87°/3 mm., d_0^{20} 1·044; *butyrate*, b. p. 102—104°/4 mm., d_0^{20} 1·012; *valerate*, b. p. 97—99°/2 mm., d_0^{20} 0·999; *benzoate*, b. p. 138—140°/2 mm., d_0^{20} 1·137, and *furoate*, b. p. 136—138°/3 mm., d_0^{20} 1·194. H. E. F. Notton.

α-Furfuryl chloride (2-chloromethylfuran). α-Furfuryl ethers. I. W. R. Kirner (J. Amer. Chem. Soc., 1928, **50**, 1955—1961).—*α-Furfuryl chloride*, b. p. 49·1—49·4°/26 mm., d_4^{20} 1·1783, n_D^{20} 1·4941, is prepared in 63% of the theoretical yield from α-furfuryl alcohol and thionyl chloride in pyridine at 0—15° (cf. Darzens, A., 1911, i, 513). It is more stable than the corresponding bromide (cf. Zanetti, A., 1927, 570; Gilman and Vernon, A., 1925, i, 53), remaining nearly colourless for several days after preparation. With alcohols and potassium hydroxide in ether it gives high yields of α-furfuryl ethers, for which the following new or revised data are given : methyl ether, d_4^{20} 1·0163, n_D^{20} 1·4570; ethyl, d_4^{20} 0·9844, n_D^{20} 1·4523; *n*-propyl, d_4^{20} 0·9656, n_D^{20} 1·4523; *n*-butyl, d_4^{20} 0·9516, n_D^{20} 1·4522; *allyl*, b. p. 173·5—174·5°/772 mm., d_4^{20} 1·0025, n_D^{20} 1·4718; benzyl, b. p. 108—109°/1 mm., d_4^{20} 1·0865, n_D^{20} 1·5372; α-furfuryl, b. p. 88—89°/1 mm., d_4^{20} 1·1405, n_D^{20} 1·5088; and cinnamyl, d_4^{20} 1·0802, n_D^{20} 1·5661. H. E. F. Notton.

α-Furfurylamines. J. E. Zanetti and C. O. Beckmann (J. Amer. Chem. Soc., 1928, **50**, 2031—2033).—Mono-, di-, and tri-α-furfurylamine hydrobromides are formed when a mixture of ethereal α-furfuryl bromide (A., 1927, 570) and saturated alcoholic ammonia is kept for several days at the ordinary temperature. The free amines are distilled to remove α-furfurylamine, the residue is purified through its hydrochloride and fractionally redistilled, giving *di-α-furfurylamine*, b. p. 102—103°/1 mm. [*hydrochloride*, m. p. 186—187° (cf. Williams, this vol., 183); *chloroplatinate*; *chloroaurate*], and *tri-α-furfurylamine*, b. p. 136—138°/1 mm. (*hydrochloride*, m. p. 156—157°; *chloroplatinate*; *chloroaurate*). H. E. F. Notton.

Absorption spectra of sulphonefluorescein and some derivatives. R. C. Gibbs and C. V. Shapiro (J. Amer. Chem. Soc., 1928, **50**, 1755—1762).—The absorption spectrum of 2 : 4-dihydroxybenzoylbenzene-*o*-sulphonic acid is similar to those of benzaldehyde, acetophenone, and 2 : 4-dihydroxybenzoyl-*o*-benzoic acid (cf. this vol., 526), which indicates a ketonic structure for this acid. The absorption spectra of sulphonefluorescein and dibromosulphonefluorescein in alcohol are unaffected by addition of hydrogen chloride; they differ from that of fluorescein, but correspond closely with that of fluorescein hydrochloride. Accordingly, the sulphonefluoresceins probably exist in the free state as internal salts of *p*-quinonoid structure. A similar difference is shown to exist between the quinonoid curves for sulphonefluorescein and dibromosulphonefluorescein diacetates and the lactonoid curves for 3 : 6-dichlorosulphonefluoran and fluorescein diacetate. The absorption spectra of resorcinolbenzein, fluorescein, sulphonefluorescein, and dibromosulphonefluorescein in sulphuric acid show a remarkable similarity in type, as do those of the first three in alcoholic potassium hydroxide (4 mols.). The relative positions of corresponding bands are in accordance with the rule that increase in the mol. wt. displaces the band towards the red. With 1 mol. of alcoholic potassium hydroxide the curve for sulphonefluorescein partly resembles that for free fluorescein. In 33% aqueous potassium hydroxide sulphonefluorescein changes in the same way as fluorescein, the initially orange solution becoming purple (opening of the pyrone ring) after several days, and pale pink (irreversible decomposition) after 8 months. Opening of the pyrone ring does not greatly affect the position of the bands, but alters their relative intensity. H. E. F. Notton.

Quinolsulphonephthalein and some derivatives. W. R. Orndorff and C. V. Shapiro (J. Amer. Chem. Soc., 1928, **50**, 1730—1734).—When quinol and *o*-sulphobenzoic anhydride are fused together at 130° for 18—24 hrs., dark red *quinolsulphonephthalein* (20% yield), m. p. above 300°, is formed. The substance described by Sohon (A., 1898, i, 428) was probably an amorphous by-product. Addition of dehydrating agents lowers the yield. Quinolsulphonephthalein forms a bluish-purple *mono*- and bluish-black (?) *tri-ammonium* salt, a bluish-purple *disodium* salt, brown *barium* salt, and yellow *dibenzoate*. Unlike quinolphthalein, it does not yield colourless lactonoid derivatives or combine with hydrogen chloride. These facts and the spectrochemical properties of quinolsulphonephthalein indicate that it is an internal salt of *m*-quinonoid structure (annexed formula). H. E. F. Notton.

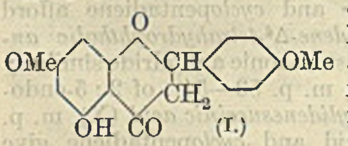


Spectrographs of compounds of the flavone series. I. Derivatives of flavone, flavonol, and styrylchromonol. II. Synthesis of two new flavone glucosides. Spectrographical influence of sugar combination and acylation. S. Hattori (Acta Phytochim., 1928, 4, 41—61, 63—75).—I. The spectrographs have been obtained of a number of flavones and related compounds, some of which were synthesised previously (A., 1927, 883). Introduction of a hydroxyl group into the benzopyrone nucleus of flavone has a much greater influence than introduction into the side benzene ring, except with 4′-hydroxyflavone, where the influence of the hydroxyl group is very marked. Methoxyl and ethoxyl groups are optically equivalent to the hydroxyl group, and a methylenedioxy-, two adjacent hydroxyl groups, and adjacent methoxyl and ethoxyl groups are equivalent. The auxochromic influence of hydroxyl is destroyed by acetylation. The introduction of methyl into the benzene ring of flavone (*e.g.*, 6-methylflavone) does not alter the absorption spectrum. The absorption spectra of some styrylchromonols and benzylchromonols (cf. Robinson and Shinoda, A., 1925, i, 1301) and the preparation of 2-*hydroxy*-3′-*methoxy*-4′-*ethoxystyryl methyl ketone*, m. p. 107°, 3′-*methoxy*-4′-*ethoxyflavanone*, m. p. 141°, 3′-*methoxy*-4′-*ethoxyflavone*, m. p. 168°, and 3′-*methoxy*-4′-*ethoxyflavanol*, m. p. 169°, are given.

II. Hydroxyflavone in potassium hydroxide solution treated with an acetone solution of acetobromoglucose yields 7-*tetra-acetylglucosidoxyflavone*, m. p. 183°, which when dissolved in methyl alcohol and dry ammonia gas passed in, yields 7-*glucosidoxyflavone*, m. p. 255°, $[\alpha]_D$ $-160{\cdot}42°$ (in methyl alcohol). 4′-Hydroxyflavone similarly yields 4′-*tetra-acetylglucosidoxyflavone*, m. p. 216—217°, and 4′-*glucosidoxyflavone*, m. p. 252—254° (lævorotatory but $[\alpha]_D$ not determined). The preparation of 7-*propionyloxyflavone*, m. p. 104°, and 7-*hexoyloxyflavone*, m. p. 82—83°, is described. 7-Hydroxyflavone, its glucoside, and the acetylglucoside have the same spectrographs and a similar agreement is obtained with 4′-hydroxyflavone and its derivatives. The glucosidoxyl and alkoxyl groups are spectrographically equivalent to the hydroxyl group, whereas an acyl group completely abolishes the effect of the hydroxyl group. It is suggested, therefore, that the position of the glucoside linking in compounds of this type may be determined by acetylating the glucoside and comparing the absorption curve with those of the acetates of the seven isomeric hydroxyflavones.

A. Wormall.

Flavanone glucosides. II. Constitution of naringenin. Y. Asahina and M. Inubuse (Ber., 1928, **61**, [*B*], 1514—1516).—Naringin, m. p. 82°, $[\alpha]_D^{19}$ $-82{\cdot}11°$ in alcohol, is obtained by extracting the dried blossoms of *Citrus decumana* with hot alcohol, evaporation of the solution, and crystallisation of the residue from water. It is converted by boiling, dilute sulphuric acid into naringenin, m. p. 248°. The latter substance is converted by acetic anhydride containing a trace of sulphuric acid into its *triacetate*, $C_{15}H_9O_5Ac_3$, m. p. 53—55°, which does not give a coloration with ferric chloride, but affords a red colour when reduced with magnesium and hydrochloric acid. Prolonged ebullition with acetic anhydride and sodium acetate yields a *tetra-acetate*, $C_{15}H_8O_5Ac_4$, m. p. 133—136°, which does not give a colour when reduced. Methylation with diazomethane transforms naringenin into its dimethyl ether, m. p. 116—117°, identical with sakuranetin monomethyl ether (I). Naringenin is therefore 5 : 7 : 4′-trihydroxyflavanone. H. Wren.


(I.)

Synthesis of anthocyanins. IV. Constitution of *O*-benzoylphloroglucinaldehyde. A. Robertson, R. Robinson, and (Miss) A. M. Struthers (J.C.S., 1928, 1455—1459).—The constitution of the product of benzoylation of phloroglucinaldehyde by the Schotten–Baumann method (A., 1927, 974) was shown to be 2-benzoyloxy-4 : 6-dihydroxybenzaldehyde. It could be prepared by application of the

Gattermann synthesis to *O*-benzoylphloroglucinol, and it could be methylated by means of methyl iodide and potassium carbonate in acetone, giving 2-*benzoyloxy*-4 : 6-*dimethoxybenzaldehyde*, m. p. 148° (+$0{\cdot}5H_2O$), also obtained from 2-hydroxy-4 : 6-dimethoxybenzaldehyde. The last compound was obtained by hydrolysis of the benzoyl derivative and yielded *O*-pentamethylcyanidin chloride [*ferrichloride*, m. p. 210° (after softening)]. Further, the benzoylacacetinidin chloride (7-hydroxy-5-benzoyloxy-4′-methoxyflavylium chloride) [*picrate*, m. p. 230—231° (decomp., darkening at 215°)], obtained previously from *O*-benzoylphloroglucinaldehyde and *p*-acetylanisole (A., 1927, 1083), was also prepared from *O*-benzoylphloroglucinol and anisoylacetaldehyde. Moreover, benzoylacacetinidin chloride yields a red anhydro-base, whilst the anhydro-bases from 5-monohydroxylated flavylium salts are blue or violet. 5-*Hydroxy*-4′-*methoxy*-6 : 8-*dimethylflavylium chloride* (+$3H_2O$) was obtained by condensation of *m*-xylorcylaldehyde and *p*-acetylanisole in formic acid, and yielded a colour-base giving a blue solution in benzene. 5-Hydroxy-3 : 3′ : 4′-trimethoxy-6 : 8-dimethylflavylium chloride (A., 1927, 1064) yielded similarly a bluish-violet colour-base. Acetylation and reduction of 5-hydroxy-7-methoxy- and 7-hydroxy-4′-methoxy-flavones yielded violet and red colour-bases, respectively, supporting the general rule.

R. K. CALLOW.

Pigment of elderberry (*Sambucus nigra*, L.). T. J. NOLAN and M. T. CASEY (Proc. Roy. Irish Acad., 1928, 38, 93—99; cf. Karrer and Widmer, A., 1927, 252).—The colouring matter of elderberry skins was extracted by ethyl-alcoholic hydrochloric acid. The *anthocyanin chloride* (*picrate*) so obtained is a brown powder (cf. *loc. cit.*), readily soluble in water (orange-red), methyl alcohol (violet-red), and dilute mineral acids. When hydrolysed with hot hydrochloric acid it yields an *anthocyanidin chloride* (*sulphate*; *picrate*) which is almost insoluble in cold water, is transformed by the action of warm water into an insoluble, violet product, and does not contain methoxyl. Colour reactions of the anthocyanin and anthocyanidin chlorides with several reagents are given.

H. BURTON.

Condensation of aldehydes and phenols. III. Nitrated *ms*-phenyldinaphthaxanthens. O. DISCHENDORFER and E. NESITKA (Monatsh., 1928, 50, 16—39).—M.-p. curves for mixtures of *p*-nitrobenzaldehyde and β-naphthol show the existence of an intensely yellow molecular *compound* (1 : 1), m. p. 76·5°, which is readily isolated and is stable for 24 hrs. at 0°, but rapidly becomes white at 15°, especially in presence of dilute acid, reverting to the yellow form above 55°. *o*-Nitrobenzaldehyde and β-naphthol give no molecular compound (eutectic, m. p. 31·5°, with 23% of β-naphthol). With 1-bromo-β-naphthol, *p*-nitrobenzaldehyde forms a stable, yellow molecular *compound* (1 : 1), m. p. 61°. *ms*-*p*-Nitrophenyl-β-dinaphthaxanthen (Zenoni, A., 1894, i, 136), m. p. 318°, prepared by warming β-naphthol (2 mols.) and *p*-nitrobenzaldehyde in hydrochloric–acetic acid, is oxidised with manganese dioxide, lead peroxide, or sulphuric acid to the *xanthhydrol*, m. p. 297° [*ferrichloride*, m. p. 290° (decomp.); *methyl ether*, m. p. 263° (decomp.); *ethyl ether*, m. p. 243—244° (decomp.)]. Werner's so-called ether of *ms*-phenyl-β-dinaphthaxanthhydrol is shown to be the xanthhydrol itself. By passing dry hydrogen chloride into a solution of the nitroxanthhydrol in chloroform containing a little acetyl chloride, ms-p-*nitrophenyl*-β-*dinaphthaxanthylium chloride hydrochloride* [*mercurichloride*, m. p. 253° (decomp.)] is obtained as red crystals rapidly becoming reddish-violet by loss of hydrogen chloride. The xanthylium *perbromide* and *perchlorate* (decomp. 299—301°) are described.

ms-*p*-Nitrophenyl-β-dinaphthaxanthen gives by reduction with zinc dust and acetic acid the p-*acetamidophenyl* compound, m. p. 170° (decomp., re-melting at 246°), from which are obtained by hydrolysis ms-p-*acetamidophenyl*-β-*dinaphthaxanthen*, m. p. 253—254° (decomp.), or by oxidation ms-p-*acetamidophenyl*-β-*dinaphthaxanthhydrol*, m. p. 270° [decomp.; *ferrichloride*, m. p. 243—245° (decomp.); *perchlorate*, m. p. 260° (decomp.); *mercurichloride*, m. p. 200—205° (decomp.)]. Nitration of the nitrophenylxanthen or of the xanthhydrol gives a *dinitro*-ms-p-*nitrophenyl*-β-*dinaphthaxanthhydrol*, darkening at 250° and not melted at 380°, in which, since it differs from the dinitrated *ms*-*o*-nitrophenyl compound (Dischendorfer, A., 1927, 1201), the new nitro-groups have not entered the phenyl nucleus. The corresponding *ferrichloride*, m. p. 325° (decomp.), *perbromide*, m. p. 260—270° (decomp.), and *perchlorate*, m. p. 301° (decomp.), are described. Nitration of *ms*-phenyl-β-dinaphthaxanthen or, better, of the xanthhydrol gives *dinitro*-ms-*phenyl*-β-*dinaphthaxanthhydrol*, m. p. 297—298° (decomp.), from which the xanthylium *ferrichloride*, m. p. 260° (decomp.), *perchlorate*, m. p. 288° (decomp.), and *perbromide* are prepared.

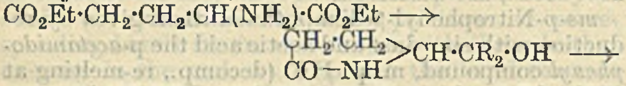
2 : 4 : 6-Trinitrobenzaldehyde forms with β-naphthol a molecular *compound* (1 : 1), m. p. 153°. Oxidation of *p*-dimethylaminophenyldi-(2-hydroxy-α-naphthyl)-methane (Hewitt, Turner, and Bradley, J.C.S., 1902, 81, 1207) with hypobromite gives a *dehydro*-compound, $C_{29}H_{23}O_2N$, m. p. 245°.

C. HOLLINS.

Preparation and properties of selenophen and certain halogen derivatives of selenophen. H. V. A. BRISCOE and J. B. PEEL (J.C.S., 1928, 1741—1747).—When acetylene was passed over selenium at 400° (a solid deposit which appeared in the reaction-tube apparently exerted a catalytic effect), naphthalene, other hydrocarbons, and *selenophen*, b. p. 110°/752 mm., f. p. −38°, were obtained. The density, vapour density, and surface tension were determined over ranges of temperature: d_4^{15} 1·5307, coefficient of expansion, 3α (15—50°) 0·001045, n_D^{15} 1·568, γ (15°) 36·49 dynes/cm. Vapour density and cryoscopic determinations agreed with the formula C_4H_4Se. The substance was stable and unaffected by oxidising or reducing agents, or by boiling with water, sodium hydroxide solution, or concentrated hydrochloric acid. With sulphuric acid and isatin an "indophenin" reaction was produced. Nitration and sulphonation yielded tarry products. Bromination in carbon disulphide yielded *tetrabromoselenophen*, m. p. 102°. Chlorination gave a small yield of *tetrachloroselenophen*, m. p. 87° (decomp.), which was markedly less stable than the bromo-derivative, being decomposed by warming with water or on keeping. The "selenophen" described by Foa (A., 1910, i, 187) had entirely different properties.

R. K. Callow.

Synthesis of hydroxyamino-acids. S. Kanao and S. Inagawa (J. Pharm. Soc. Japan, 1928, No. 554, 355—358; cf. *ibid.*, No. 553, 238—252).—α′-(2-Pyrrolidonyl)dialkylcarbinols, which were obtained from ethyl glutamate and organo-magnesium halides, can be readily hydrolysed into γ-amino-δ-hydroxy-δδ-dialkylvaleric acids, thus:



$$CO_2Et\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2Et \longrightarrow {\begin{matrix}CH_2\cdot CH_2\\ |\\ CO-NH\end{matrix}}\!\!>\!CH\cdot CR_2\cdot OH \longrightarrow$$

$OH\cdot CR_2\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO_2H$. *l*-α-(2-Pyrrolidonyl)diethylcarbinol, when boiled with 20% barium hydroxide solution, gives *γ-amino-δ-hydroxy-δδ-diethylvaleric acid*, m. p. 143°, $[\alpha]_D^{20}$ +3·4° (in water), $[\alpha]_D^{20}$ −14·5° (in 0·3*N*-hydrochloric acid). α-(2-Pyrrolidonyl)dibutylcarbinol is stable to baryta, but when hydrolysed with alcoholic potassium hydroxide, it gives *γ-amino-δ-hydroxy-δδ-dibutylvaleric acid*, m. p. 147°. α-(2-Pyrrolidonyl)diphenylcarbinol similarly gives *γ-amino-δ-hydroxy-δδ-diphenylvaleric acid*, m. p. 204—205°, $[\alpha]_D^{20}$ +48·5° (in 5*N*-acetic acid).

K. Ishimura.

Natural rotation of polarised light by optically active bases. I. Influence of solvent on the rotation of *d*-α-pipecoline and its hydrochloride. W. Leithe (Monatsh., 1928, 50, 40—47).—Solvents may be grouped in three classes according as they have a very small, an appreciable, or a considerable influence on the rotatory power of *d*-α-pipecoline ($[\alpha]_D^{15}$ +36·0° in liquid state). In the first class are piperidine, hexane, and ether, and the absence of any appreciable effect is due to small associating power and to small effect of neighbouring solvent molecules on the field surrounding each molecule of solute. The influence is always markedly small in the case of solvents closely related to the solute, *e.g.*, piperidine in the present instance, and generally when racemics are the solvents for corresponding active compounds (cf. Ladenburg, A., 1910, i, 696). In the second class are benzene, ethyl acetate, acetone, pyridine, carbon tetrachloride, and chloroform, which do not (as judged by density determinations) form compounds with *d*-α-pipecoline, but probably have some tendency in that direction or influence the field by their residual affinity. The third class includes ethyl and methyl alcohols, water, and glacial acetic acid; these all produce marked effect also on the density, and their influence is due to formation of compounds.

C. Hollins.

Pentadecoyl-lutidine and pentadecoyl-lupetidine, a higher homologue of coniine. S. Gottfried and F. Ulzer (Wiss. Mitt. Oesterr. Heilmittelstelle, 1926, No. 1, 1—3, No. 2, 1—4; 1927, No. 3, 1—3, No. 4, 1—4; Chem. Zentr., 1928, i, 1192—1193).—A mixture of monomeric and trimeric palmitaldehyde, b. p. 170—172°/8 mm., 240—241° (corr.)/100 mm., m. p. 57·5—58·5°, was obtained from barium palmitate, formate, and carbonate; treatment with hydroxylamine in 80% alcohol yields palmitaldoxime, m. p. 87·5—88°, and leaves the trimeric aldehyde, m. p. 72·5°. The monomeric aldehyde has m. p. 33·5—34° (confirming Le Sueur's observation). The mixture, m. p. 58°, cannot be depolymerised by simple distillation; it was heated at 150°, 1—2 mg. of zinc chloride were added, and the mixture was rapidly distilled in a vacuum. When heated with ethyl acetate and alcoholic ammonia, the monomeric aldehyde affords *ethyl* 4-*pentadecoyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*carboxylate*, m. p. 50·5—51°. The crude product is treated with nitrogen trioxide, followed by treatment with hydrochloric acid and then sodium hydroxide, yielding *ethyl* 4-*pentadecoyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, b. p. 267—269°/10 mm. (*hydrochloride*, m. p. 88—89°; *chloroplatinate*, m. p. 119—120·5°). The free *acid* has m. p. 61° [*hydrochloride*, m. p. 123—124° (decomp.); *lead*, *silver*, and *copper* salts]. Distillation of the hydrochloride with soda-lime affords pentadecoyl-lutidine [4-*pentadecoyl*-2 : 6-*dimethylpyridine*], b. p. 240—242°/10 mm. (*hydrochloride*, m. p. 78—79°; *chloroplatinate*, m. p. 107—108°; *picrate*, m. p. 71°), which with sodium and alcohol gives pentadecoyl-lupetidine [4-*pentadecoyl*-2 : 6-*dimethylpiperidine*], an oil [*hydrochloride*, m. p. 126° (decomp.); *chloroplatinate*, m. p. 145·5—146·5°].

A. A. Eldridge.

Manufacture of alkyl and aralkyl derivatives of diphenolisatins. F. Hoffmann-La Roche & Co.—See B., 1928, 548.

Decahydroquinolone derivatives. III. Hofmann degradation of decahydroquinoline. S. Fujise (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 185—195; cf. this vol., 898).—*trans*-Decahydroquinoline, m. p. 45—45·5°, with methyl iodide and alkali yielded trans-N-*methyldecahydroquinolone methiodide*, m. p. 276° (*methochloroplatinate*, m. p. 255—256°; *methochloroaurate*, m. p. 172—173°), which when treated with silver hydroxide and distilled gave a 76% yield of a *base*, $C_{11}H_{21}N$, b. p. 204—205° (*picrate*, m. p. 101—102°). With platinum- or palladium-black and hydrogen the latter afforded trans-2-*dimethylamino*-n-*propyl*cyclo*hexane*, b. p. 206—208°, n_4^{20} 1·46036, d_D^{20} 0·8551 (*picrate*, m. p. 114·5—115·5°; *chloroaurate*, m. p. 146—147°). Further degradation of the latter was effected by conversion into the *methiodide*, m. p. 185° (*methchloroaurate*, m. p. 94—95°), which gave (silver hydroxide; distillation) a *hydrocarbon*, C_9H_{16}, probably Δ^2-n-*propyl*cyclo*hexene*, b. p. 154·5—155·5°, d_4^{19} 0·8162, n_D^{19} 1·4541, and some 2-dimethylamino-*n*-propyl*cyclo*hexane. In a similar manner *cis*-decahydroquinoline, b. p. 205°, was converted into cis-N-*methyldecahydroquinoline methiodide*, m. p. 260° (*methochloroaurate*, m. p. 223°, *methochloroplatinate*, m. p. 254°), and the latter into an unsaturated *base* (60% yield), $C_{11}H_{21}N$, b. p. 213—214° (*picrate*, m. p. 135—138°), which when reduced with platinum-black and hydrogen gave cis-2-*dimethylamino*-n-*propyl*cyclo*hexane*, b. p. 214—216° (*picrate*, m. p. 173°; *chloroaurate*, m. p. 132°; *methiodide*, m. p. 186°; *methochloroaurate*, m. p. 130°).

I. Vogel.

αγ-Diamino-β-phenylpropane and related compounds of pharmacological interest. J. G. Jackson and J. Kenner (J.C.S., 1928, 1657—1662).—The pressor influence of β-phenylethylamine and the depressor influence of polymethylenediamines are approximately balanced in derivatives of αγ-diamino-β-phenylpropane, but in the 4-aminomethyldihydroisoquinoline derivatives obtained by intramolecular condensation the effect of the dihydro*iso*quinoline structure is preponderant, and they cause definite depression of the blood pressure of the cat.

Ethyl β-*phenylglutarate*, b. p. 180—184°/14 mm., was converted into β-*phenylglutardihydrazide*, m. p. 177°. The *diurethane*, m. p. 73—74°, was obtained by the action of amyl nitrite and hydrogen chloride, and converted by boiling hydrobromic acid into *αγ-diamino-β-phenylpropane hydrobromide*, m. p. 252° (decomp. 272°) [*base*, b. p. 150°/15 mm.; *carbonate*, m. p. 172° (decomp.); *picrate*, m. p. 247° (decomp.)]. The following derivatives were prepared: *diacetyl-*, m. p. 153—154°, *dibenzoyl-*, m. p. 179°, *di-*p-*toluenesulphonyl-*, m. p. 91°, NN′-*dimethyl*-NN′-*di*-p-*toluenesulphonyl-*, m. p. 60°, *hydrochloride* of NN′-*dimethyl-*, m. p. 249°. *γ-Amino-β-phenylbutyric acid hydrobromide*, m. p. 114°, obtained as a by-product in the preparation of αγ-diamino-β-phenylpropane, yielded with alkali 4-*phenyl*-2-*pyrrolidone*, m. p. 60° (*acetyl* derivative; m. p. 63°, *benzoyl* derivative, m. p. 145°). αγ-Diacetamido-β-phenylpropane, when boiled with phosphoric oxide in toluene, furnished 4-*aminomethyl*-1-*methyl*-3 : 4-*dihydro*isoquinoline, m. p. 182° (*dihydrochloride*, m. p. 222°). αγ-Dibenzamido-β-phenylpropane yielded the *benzoyl* derivative, m. p. 114°, of 4-*aminomethyl*-1-*phenyl*-3 : 4-*dihydro*isoquinoline, m. p. 169° (*dihydrochloride*, m. p. 291°). Condensation of ethyl *p*-methoxycinnamate with ethyl malonate furnished *ethyl* p-*methoxyphenylpropane-ααγ-tricarboxylate*, b. p. 225—240°/12 mm., which, on hydrolysis and heating, yielded β-p-*methoxyphenylglutaric acid*, m. p. 165° (*anhydride*, m. p. 152°; *methyl* ester, m. p. 42°, b. p. 205—210°/20 mm.; *ethyl* ester, b. p. 206—210°/14 mm.; *dihydrazide*, m. p. 190°; *diurethane*, m. p. 99—100°). Hydrolysis by hydrobromic acid yielded *αγ-diamino-β-*p-*hydroxyphenylpropane dihydrobromide*, m. p. 316° (*tribenzoyl* derivative of the base, m. p. 206—207°). The following are also described: 3 : 4-*dimethoxybenzylidenemalonic acid*, m. p. 208° (decomp.), *ethyl* β-3 : 4-*dimethoxyphenylglutaric acid*, m. p. 125—130° (+H_2O) (*anhydride*, m. p. 124°; *methyl* ester, m. p. 73°; *ethyl* ester, b. p. 226—229°/15 mm.; *dihydrazide*, m. p. 182°), *αγ-diamino-β-3 : 4-dihydroxyphenylpropane dihydrobromide* (+H_2O), m. p. 294° (anhydrous) (*tetrabenzoyl* derivative, m. p. 217°).

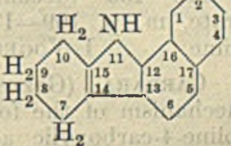
R. K. CALLOW.

Condensation of hexahydrocarbazole and of tetrahydropentindole with *cyclo*pentanone cyanohydrin. S. G. P. PLANT and (MISS) D. M. L. RIPPON (J.C.S., 1928, 1906—1913).—An attempt was made to synthesise ring structures of the type present in 8 : 9-(1′ : 2′-*cyclo*hexyl)hexahydrocarbazole (cf. Manjunath, A., 1927, 978) by a method analogous to the preparation of carbazole by fusion of 1-anilino*cyclo*pentane-1-carboxylic acid with potassium hydroxide (Plant and Facer, A., 1925, i, 1271). The reactions did not, however, go in the expected directions. Treatment of hexahydrocarbazole with *cyclo*pentanone and potassium cyanide in glacial acetic acid yielded 1-*cyano*-1-(9′-*hexahydrocarbazyl*)cyclo*pentane*, m. p. 76°. Aqueous or alcoholic hydrochloric acid decomposed this into *cyclo*pentanone and hexahydrocarbazole, but cold, concentrated sulphuric acid yielded 1-(9′-*hexahydrocarbazyl*)cyclo*pentane*-1-*carboxylamide*, m. p. 160°, which could not be hydrolysed to the acid by the action of aqueous-alcoholic potassium hydroxide or aqueous sulphuric acid. When boiled with hydrochloric acid or heated with solid potassium hydroxide the amide decomposed with the formation of hexahydrocarbazole. Reduction of the nitrosoamine of 1-anilino*cyclo*pentane-1-carboxylic acid by zinc and acetic acid in the presence of *cyclo*hexanone yielded 1-(9′-*tetrahydrocarbazyl*)cyclo*pentane*-1-*carboxylic acid*, m. p. 184°, which, when warmed with 60% aqueous sulphuric acid, distilled, or heated with solid potassium hydroxide, yielded tetrahydrocarbazole and Δ^1-*cyclo*pentene-1-carboxylic acid. It could not be reduced to the corresponding hexahydrocarbazole derivative.

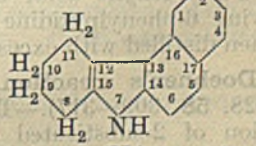
Electrolytic reduction of dihydropentindole (Perkin and Plant, J.C.S., 1923, **123**, 3242) yielded *tetrahydropentindole*, b. p. 152°/16 mm., m. p. 21° (8-*acetyl* derivative, m. p. 78°; 8-*benzoyl* derivative, m. p. 86°; *picrate*, m. p. 159°), which was certainly the *cis*-form. Methyl iodide yielded the 8-*methyl* derivative, b. p. 136—137°/15 mm. (*picrate*, m. p. 116°; *methiodide*, m. p. 189°). 1-*Cyano*-1-(8′-*tetrahydropentindyl*)-cyclo*pentane*, m. p. 51° (*picrate*, m. p. 126°), and 1-(8′-*tetrahydropentindyl*)cyclo*pentane*-1-*carboxylamide*, m. p. 130°, were obtained in a similar way to the hexahydrocarbazole derivatives. They decomposed under similar conditions to yield *cyclo*pentanone and tetrahydropentindole.

R. K. CALLOW.

Derivatives of 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole and of 8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole. S. H. OAKESHOTT and S. G. P. PLANT (J.C.S., 1928, 1840—1847).—7 : 8 : 9 : 10-Tetrahydro-αβ-naphthacarbazole ($\Delta^{1(6)}$-tetrahydrobenzo-α-naphthindole; cf. Borsche, Witte, and Bothe, A., 1908, i, 365) (I) (*picrate*, m. p. 172°) yielded αβ-naphthacarbazole on dehydrogenation with sulphur. Acetylation, which could be carried out only by the action of acetyl chloride on the Grignard compound, yielded the 11-*acetyl* derivative, m. p. 125°. The 11-*benzoyl* derivative, m. p. 146—147°, was obtained similarly, and on nitration gave a *trinitro*-11-*benzoyl* derivative, m. p. 255°. This was the only crystalline nitration product isolated from (I) or its derivatives. Electrolytic reduction of (I) yielded the 7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-compound, m. p. 88° (*dinitro*-derivative, m. p. 139—140°; 11-*acetyl* derivative, m. p. 132°, and 11-*benzoyl* derivative, m. p. 148—149°, prepared by usual methods).



(I.)



(II.)

8 : 9 : 10 : 11 - Tetrahydro - α′β′ - naphthacarbazole ($\Delta^{1(6)}$-tetrahydrobenzo-β-naphthindole) (II), m. p. 137° (Borsche, *loc. cit.*, gives 152°), yielded a *picrate*, m. p. 194° (decomp.). Dehydrogenation yielded α′β′-naphthacarbazole, confirming the constitution. Acetic anhydride and a trace of sulphuric acid yielded

first the 7-*acetyl* derivative, m. p. 162° (also prepared by way of the Grignard compound), and then a C-*acetyl*-7-*acetyl* derivative, m. p. 185°, which was hydrolysed by aqueous potassium hydroxide to a C-*acetyl* derivative, m. p. 213° (*oxime*, m. p. 213—216°). The following derivatives were also prepared: *mononitro*-7-*acetyl*, m. p. 222°; 7-*benzoyl*, m. p. 139°; *mononitro*-7-*benzoyl*, m. p. 208—209°. Reduction of (II) by red phosphorus and hydriodic acid yielded the 8 : 9 : 10 : 11 : 12 : 15-*hexahydro*-compound, b. p. 198—202°/10 mm. (*hydrochloride*, m. p. 265°; 7-*acetyl* derivative, m. p. 120°; 7-*benzoyl* derivative, m. p. 131°). From neither (I) nor (II) or their derivatives could any products resulting from the addition of $\cdot OH$ and $\cdot NO_2$ or $\cdot OH$ and $\cdot OH$ to the double linking (as in the case of tetrahydrocarbazole) be isolated. The hexahydro-compounds are undoubtedly *cis*-forms.

R. K. CALLOW.

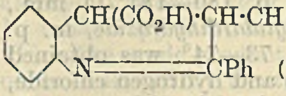
Chlorination of 2-aminopyridine. A. E. TSCHITSCHIBABIN and A. F. EGOROV (J. Russ. Phys. Chem. Soc., 1928, **60**, 683—690).—Chlorination of 2-amino-pyridine with a large excess (97%) of chlorine gave an 80% yield of 3 : 5-dichloro-2-aminopyridine, m. p. 80—81°, and 68% of 5-chloro-2-aminopyridine, m. p. 134—135°. Treatment of the latter with a mixture of concentrated nitric and sulphuric acids at 0° yielded 5-chloro-2-nitroaminopyridine, m. p. 159—160°, which when warmed with concentrated sulphuric acid to 55° and treated with iced water isomerised to 5-chloro-3-nitro-2-aminopyridine, m. p. 195—196°. Diazotisation of the chloropyridine followed by hydrolysis gave 5-chloro-2-hydroxypyridine, m. p. 163°. Under similar conditions, the dichloro-compound yielded the corresponding 3 : 5-dichloro-2-hydroxypyridine. If hydrochloric acid was used in the above diazotisations instead of sulphuric acid, 2 : 5-dichloropyridine and 2 : 3 : 5-trichloropyridine were respectively obtained.

M. ZVEGINTZOV.

New synthesis of pyridine derivatives. E. SPÄTH and G. BURGER (Monatsh., 1928, **49**, 265—270).—Condensation of benzoylacetaldehyde and ethyl aminocrotonate in ethereal solution gave *ethyl* 6-*phenyl*-2-*methylpyridine*-3-*carboxylate* (I) (*chloroplatinate*, m. p. 201—203°) and none of the expected 4-phenyl-2-methyl derivative. Hydrolysis of (I) with aqueous potassium hydroxide led to 6-*phenyl*-2-*methylpyridine*-3-*carboxylic acid* (II), m. p. 196° [*hydrochloride*, m. p. 288° (decomp.)], from which 6-phenyl-2-methylpyridine (cf. Scholtz, A., 1895, i, 562) was obtained by distillation with lime. Oxidation of (II) with alkaline permanganate led to 6-*phenylpyridine*-2 : 3-*dicarboxylic acid*, m. p. 148—150° (decomp.), giving 6-phenylpyridine (picrate, m. p. 169—170°) when distilled with excess of lime.

I. VOGEL.

Doebner's reaction. G. CARRARA (Gazzetta, 1928, **58**, 309—317).—The mechanism of the formation of 2-substituted quinoline-4-carboxylic acids by the condensation of benzaldehyde, an aromatic amine, and pyruvic acid (cf. Doebner, A., 1887, 504; 1888, 299) is shown to be probably as follows. The pyruvic acid (1 mol.) and benzylideneaniline (1 mol.) combine, by condensation of aldol type, to form a disubstituted propionylformic acid, $CO_2H\cdot CO\cdot CH_2\cdot CHPh\cdot NHPh$, which in cold alcohol immediately yields the corresponding lactam, 4 : 5-diketo-1 : 2-diphenylpyrrolidine, but, when heated, is transformed into the acid, $CO_2H\cdot CH(OH)\cdot CH{:}CPh\cdot NHPh$. This acid, with another molecule of benzylideneaniline, undergoes a double, cyclic-aldol condensation, yielding the unstable compound (I), which decomposes into benzylaniline and 2-phenylquinoline-4-carboxylic acid.


(I.)

That the reaction proceeds in this way is shown by the fact that, in definite conditions that render possible the rupture of the lactam ring and hence an equilibrium with the corresponding acid, $CO_2H\cdot CO\cdot CH_2\cdot CHPh\cdot NHPh$, 4 : 5-diketo-1 : 2-diphenylpyrrolidine is capable of reacting with benzylideneaniline to give 2-phenylquinoline-4-carboxylic acid.

T. H. POPE.

Synthesis of acridinic acid [quinoline-2 : 3-dicarboxylic acid]. G. KOLLER and E. STRANG (Monatsh., 1928, **50**, 48—50).—*o*-Aminobenzaldehyde is condensed with ethyl oxalacetate in absolute alcohol in presence of a little sodium hydroxide to give ethyl acridinate, m. p. 54—55°, which is hydrolysed with alkali to the acid.

C. HOLLINS.

Toxicity of an impurity in official cinchophen [2-phenylquinoline-4-carboxylic acid]. R. A. HATCHER (J. Amer. Pharm. Assoc., 1928, **17**, 557—563).—Cinchophen (U.S. Pharmacopœia) is contaminated with 3% of γ-*anilino*-γ-*phenylbutyric acid*, m. p. 193—194° (brominated *derivative*, m. p. 135°), with which it forms a *compound*, m. p. 183°. The impurity intravenously injected in large doses into cats causes increased reflex excitability, and convulsions (with probably stimulation of the vasomotor centre) and stoppage of the heart.

E. W. WIGNALL.

Carbazole-1-carboxylic acid. E. F. BRISCOE and S. G. P. PLANT (J.C.S., 1928, 1990—1991).—When a mixture of tetrahydrocarbazole-8-carboxylic acid (Collar and Plant, A., 1926, 735), sulphur, and pure quinoline is refluxed for 12 hrs. and the crude acid purified through its methyl ester, carbazole-1-carboxylic acid, identical with the acid obtained by Ciamician and Silber (A., 1882, 1103), is obtained.

J. W. BAKER.

Synthesis of acridone and acridine. G. KOLLER and E. KRAKAUER (Monatsh., 1928, **50**, 51—54).—Distillation of calcium anthranilate in a vacuum at 340° gives an *anhydro-bis*-2 : 2′-*diaminobenzophenone*, $NH_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot N{:}C(C_6H_4\cdot NH_2)_2$, m. p. 233°, which is hydrolysed by concentrated hydrochloric acid at 170° to acridone, or may be converted into acridine by distillation with zinc dust.

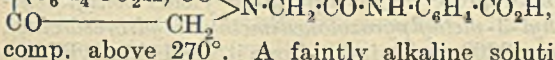
C. HOLLINS.

Derivatives of barbituric acid. A. W. DOX and E. G. JONES (J. Amer. Chem. Soc., 1928, **50**, 2033—2036).—The yield of "*tetrahydro*-α-*furanmethyl bromide*" [? tetrahydro-α-furfuryl bromide], b. p. 168—170°/744 mm., from tetrahydro-α-furfuryl alcohol by the usual methods is poor. With ethyl sodioethylmalonate the bromide forms *ethyl tetrahydrofuranmethylethylmalonate*, b. p. 155—157°/12 mm., which condenses with carbamide in presence of sodium ethoxide to *tetrahydrofuranmethylethylbarbituric acid*,

m. p. 190°. *n*-Amyl alcohol is converted by standard methods into *ethyl* n-*amylmalonate*, b. p. 134—136°/14 mm.; n-*amylmalonamide*, m. p. 206°; *chloro*-n-*amylmalonamide*, m. p. 134—135°, which is some 400 times as sweet as sucrose (cf. A., 1924, i, 716); n-*amylbarbituric acid*, m. p. 215°; *ethyl di*-n-*amylmalonate*, b. p. 158—161°/11 mm.; *di*-n-*amylbarbituric acid*, m. p. 118°; *ethyl ethyl*-n-*amylmalonate*, b. p. 139—141°/14 mm., and *ethyl*-n-*amylbarbituric acid*, m. p. 135°, which has a powerful hypnotic action. H. E. F. Notton.

Action of carbonyl chloride on polypeptide derivatives of *p*-aminobenzoic acid. Formation of 1 : 3-substituted hydantoins. C. Tropp (Ber., 1928, **61**, [*B*], 1431—1439).—Carbamide derivatives do not appear to be formed when carbonyl chloride acts on peptide compounds in which a hydrogen atom of the amino-group is replaced by the phenyl radical. The latter group renders the residual hydrogen of the amino-complex so mobile that substituted hydantoins are readily produced under the influence of carbonyl chloride. This ring closure does not, however, occur when a carbonyl group attached to a molecule containing other negative substituents is vicinal to the amino-group.

Carbonyldiglycylglycine is readily prepared in 55% yield by the action of carbonyl chloride in toluene on a solution of glycine anhydride in aqueous sodium hydroxide. *p*-Aminobenzoic acid in alkaline solution is transformed by chloroacetyl chloride in ether into p-*chloroacetamidobenzoic acid*, m. p. 257—258°, which with concentrated ammonia affords p-*aminoacetamidobenzoic acid* ($+H_2O$), m. p. 229°, with a small proportion of *imino*-p-*diacetamidobenzoic acid*, $NH(CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H)_2$, decomp. above 250°; the latter compound is the main product when a stiff paste of *p*-chloroacetamidobenzoic acid and water is mixed with concentrated ammonia. Treatment of *p*-aminoacetamidobenzoic acid dissolved in sodium hydroxide with carbonyl chloride in toluene yields 3-p-*carboxyphenylhydantoin*, m. p. 258—260° (decomp.). Under similar conditions, imino-*p*-diacetamidobenzoic acid affords 3-p-*carboxyphenyl*-1-*hydantoylacet*-p′-*carboxyphenylamide*,



$$\begin{array}{l}N(C_6H_4{\cdot}CO_2H){\cdot}CO \\ CO\text{———————}CH_2\end{array}\!\!>\!N{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$$

de-comp. above 270°. A faintly alkaline solution of *p*-chloroacetamidobenzoic acid in sodium hydroxide is converted by *iso*amylamine into p-iso*amylaminoacetamidobenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}CHMe_2$, m. p. 285°. Under similar conditions, diethylamine causes complete fission of the side-chain of p-*chloroacetylglycylamidobenzoic acid* (from chloroacetyl chloride and *p*-aminoacetamidobenzoic acid) with production of *p*-aminobenzoic acid. When di*iso*amylamine is gently warmed with *p*-chloroacetylglycylamidobenzoic acid in the presence of pyridine, p-*diiso**amylaminoacetylglycylamidobenzoic acid*, m. p. 253°, results; if the acid is heated with pyridine in the absence of the base, p-*carboxyphenylamidoglycylacetylpyridinium chloride*, m. p. 258°, is produced. 3-*Carboxyphenyl*-1-iso*amylhydantoin*, m. p. 189°, is described. p-*Diglycylamidobenzoic acid*, m. p. 233°, from *p*-chloroacetylglycylamidobenzoic acid and ammonia, is converted by phenylcarbimide into p-N-*phenylureidoacetylglycylamidobenzoic acid*,

$CO_2H{\cdot}C_6H_4{\cdot}[NH{\cdot}CO{\cdot}CH_2]_2{\cdot}NH{\cdot}CO{\cdot}NHPh$, m. p. 242°.

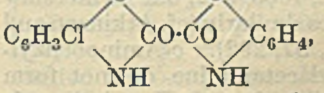
H. Wren.

Anhydrides of amino-acids. I. Molecular compounds of diketopiperazine with copper halides. T. Asahina and T. Dōno (Bull. Chem. Soc. Japan, 1928, **3**, 151—156).—Interaction of 2 : 5-diketopiperazine and cupric chloride in aqueous solution gives (80% yield) the *compound*, $C_4H_6O_2N_2,CuCl_2,2H_2O$, decomposed by hot water and alcohol, partly by the cold solvents, and when heated at 110°. Cupric bromide gives the similar *compound*, $C_4H_6O_2N_2,CuBr_2,2H_2O$ (cf. Curtius and Göbel, A., 1888, 576). Spectroscopic determinations suggest that these compounds exist to some extent in solution when cupric salt is in excess. R. Brightman.

Dipiperidyls. C. R. Smith (J. Amer. Chem. Soc., 1928, **50**, 1936—1938).—The isomeric dipiperidyls (cf. Ahrens, A., 1891, 1093; Blau, A., 1892, 1365) are conveniently obtained by hydrogenating the corresponding dipyridyls, using a platinum oxide–platinum-black catalyst in aqueous or alcoholic hydrochloric acid. Products of partial reduction were not formed. The following are described: 4 : 4′-dipiperidyl, m. p. 172° (dinitroso-derivative, m. p. 149°; *di-phenylthiourethane*, m. p. 225°); 2 : 2′-*dipiperidyl di-phenylthiourethane*, m. p. 178°; 2 : 3′-dipiperidyl picrate, m. p. 224°; 3 : 3′-*dipiperidyl*, m. p. 105°, b. p. 282° (*dinitroso*-derivative, m. p. 102°; *di-phenylthiourethane*, m. p. 200°), and 3 : 4′-*dipiperidyl*, m. p. 159°, b. p. 270° (*dinitroso*-derivative, m. p. 149°; *di-phenylthiourethane*, m. p. 202°; *picrate*, darkening from 200°; *chloroplatinate*, darkening from 235°).

H. E. F. Notton.

Chloro*iso*indigotins. A. Wahl and G. Féricéan (Ann. Chim., 1928, [x], **9**, 277—315).—The condensation products of 5- and 7-chloroisatin with oxindole and dioxindole, various chlorinated disulphoisatides, and products derived from them have been investigated. 7-Chloro- and 5-chloroisatin [prepared by a slight modification of Sandmeyer's method (A., 1919, i, 318) by substituting hydroxylaminesulphonic acid for the free base] by heating with a slight excess of dioxindole in alcohol with a few drops of piperidine of a water-bath yield, respectively, 7-, m. p. 238°, and 5-, m. p. 256°, -*chloroisatide*. Similarly by condensation with oxindole they yield 7-, m. p. 182°, and 5-, m. p. 207°, -*chloroisatan* (cf. Wahl and Hansen, A., 1924, i, 322). When the latter condensation is effected in acetic acid–hydrochloric acid solution the products are, respectively, 7-*chloro*iso*indigotin*,

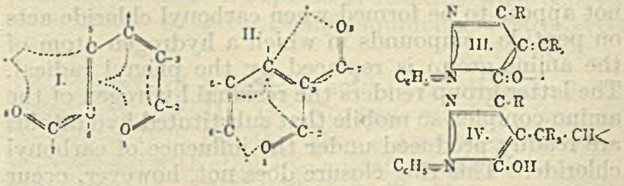


which is reduced to the *leuco*-compound with zinc and acetic acid, and 5-*chloro*iso*indigotin* (*leuco*-compound, m. p. 251°). Sulphonation of these chloro*iso*indigotins with concentrated sulphuric acid at 100° and subsequent addition of sodium chloride yields *sodium 7-chloro*-, $+H_2O$, and *sodium 5-chloro*- $+4H_2O$ (*potassium* $+3H_2O$, and *barium* $+4H_2O$ salts) -iso*indigotin*-

sulphonates. Disulphoisatide is obtained crystalline in a 90% yield by passing dry hydrogen sulphide into a suspension of isatin in anhydrous methyl alcohol at the ordinary temperature. By analysis, mol. wt. determination of the product, and a determination of the sulphur liberated in the reaction, the formula assigned to this compound by Wahl and Hansen (*loc. cit*), is confirmed and Sander's view (A., 1925, i, 977) that it is 3-thio-oxindole is excluded, since the proportion of sulphur liberated in the latter case would be double that which is actually obtained. By boiling with pyridine it yields oxindole (*benzylidene* derivative, m. p. 174°). By similar methods of preparation the yields of 7 : 7′- and 5 : 5′-dimethyldisulphoisatides (Wahl and Faivret, A., 1925, i, 588; 1926, 79) are increased to 80% and 81%, respectively, and 7 : 7′-*dichloro*- and 5 : 5′-*dichloro*- (yield 78%) -*disulphoisatides* are prepared. The action of boiling pyridine on these compounds yields, respectively, 7 : 7′-*dichloro*iso*indigotin* (*leuco*-compound by reduction) together with 7-*chloro-oxindole*, m. p. 215° (*benzylidene* derivative, m. p. 185°); and 5 : 5′-*dichloro*iso*indigotin* (*leuco*-compound) together with 5-*chloro-oxindole*, m. p. 192—195° (*benzylidene* derivative, m. p. 204—205°). By warming the 5 : 5′-dichloro-derivative with concentrated sulphuric acid the disulphonic acid is obtained from which the *disodium* $+6H_2O$, *dipotassium* $+4H_2O$, and *barium* salts are obtained.
J. W. Baker.

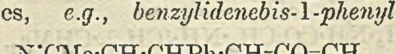
Relationship between atomic grouping and specific affinity. VII. Salt-formation capacity of glyoxaline derivatives. F. Feigl and H. Gleich (Monatsh., 1928, 49, 385—400).—Benziminazole in alcoholic solution forms the following metallic *derivatives* when treated with ammoniacal solutions of the metallic derivatives; silver salt (cf. Bamberger and Lorenzen, A., 1893, i, 433): $C_7H_5N_2HgCl$; $4C_{14}H_{10}N_4Cu,NH_3,H_2O$; $C_{14}H_{10}N_4Cd$; $C_{14}H_{10}N_4Co$, and $4C_{14}H_{10}N_4Zn,NH_3,H_2O$. Methyl- and phenyl-benziminazole form only the analogous *silver* and *mercury* derivatives. 1-Phenylbenziminazole, 1-*benzylbenziminazole*, m. p. 105° [from benzyl-*o*-phenylenediamine (cf. Kehrmann, A., 1896, i, 508), anhydrous formic acid, and ammonia], and 1 : 6-dimethylbenziminazole do not form metallic derivatives. 2-*Phenoxymethylbenziminazole* (prepared from *o*-phenylenediamine and phenoxyacetic acid), m. p. 162°, 2-*ethoxymethylbenziminazole*, m. p. 152°, and 2-*methoxymethylbenziminazole*, m. p. 137°, give *silver* and *mercury* derivatives. *o*-Phenylenecarbamide and 2-chlorobenziminazole give no metallic derivatives, whilst anhydro-oxanilide yields *mercury* and *silver* derivatives only. Amarine forms a silver salt (cf. Claus and Elbs, A., 1883, 982) but no mercury derivative; lophine behaves similarly (cf. Atkinson and Gössmann, Annalen, 1856, 97, 292). *o*-Aminobenzylaniline and *NN*′-diphenylacetamidine do not form metallic derivatives, whilst 6-methylbenziminazole and 6-*chloro*-5-*methylbenziminazole*, m. p. 191°, behave similarly to benziminazole. αβ-Naphthiminazole forms only *mercury* and *silver* derivatives. Glyoxaline yields metallic derivatives of silver (cf. Wyss, A., 1878, 25), *zinc*, and cobalt, but not of copper and cadmium.
I. Vogel.

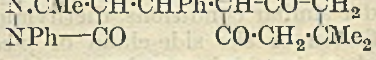
Conjugated systems. Factors disturbing valency fields. III. M. V. Ionescu (Bul. Soc. Stiinte Cluj, 1927, 3, 353—372; Chem. Zentr., 1928, i, 694; cf. this vol., 422).—A discussion of the author's results in the light of Stark's electron theory. New conjugated systems are considered: (I) in which 1 : 4- or 5 : 8-addition takes place; (II) in which 4 : 8-addition takes place. It has already been shown that αβ-unsaturated amides, unlike ketones and esters, do not add ethyl acetate or malonate. The disturbing action of the amino-group is greater than that of the alkoxyl group; the effect is annulled by suitable substitution in the amino-group. This is the case with compounds of type (III), which yield compounds of type (IV). Here the co-ordinative valencies of the amino-group are concentrated on the phenyl group and the other nitrogen atom, an effect which is increased by cyclisation, so that conjugation of the carbonyl group with the ethylene group is no longer prevented. The difference between ethyl benzylidenemalonate and benzylideneacetate is also due to the disturbing influence of the phenoxy-group. It is concluded that (1) the additive character of the various carboindogenides is diminished as the disturbing effect of the chromogen attached to the phenyl nucleus increases, and (2) for the same conjugated system and disturbing factors the change in additive properties is influenced by the nature and structure of the addenda.

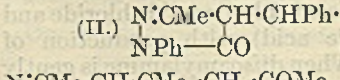


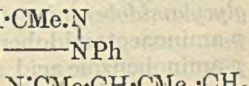
A. A. Eldridge.

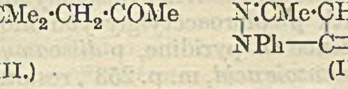
Conjugated systems. Factors disturbing valency fields. IV. Action of substances with active methylene groups on alkylidene(or arylidene)phenylmethylpyrazolones. M. V. Ionescu (Bul. Soc. Stiinte Cluj, 1927, 3, 381—393; Chem. Zentr., 1928, i, 694—695; cf. preceding abstract).—Benzylidene-1-phenyl-3-methylpyrazolone, m. p. 106°, with dimethyldihydroresorcinol in boiling absolute alcohol in presence of piperidine yields *benzylidene-1-phenyl-3-methylpyrazolonedimethyldihydroresorcinol*, (I), m. p. 220°; with indandione it yields benzylidenebis-di-indone, m. p. 256°. Hence in the formation of known alkylidene(or arylidene)bis-1-phenyl-3-methylpyrazolones, *e.g.*, *benzylidenebis-1-phenyl-3-methylpyrazolone* (II), m. p. 164—167°, from 1-phenyl-3-methylpyrazolone and aldehydes or ketones, the

(I.)

$$\begin{array}{lll}\text{N:CMe·CH·CHPh·CH–CO–CH}_2 \\ \text{NPh——CO} & & \text{CO·CH}_2\text{·CMe}_2\end{array}$$

(II.)

$$\begin{array}{lll}\text{N:CMe·CH·CHPh·CH·CMe:N} \\ \text{NPh——CO} & & \text{CO——NPh}\end{array}$$


$$\begin{array}{l}\text{N:CMe·CH·CMe}_2\text{·CH}_2\text{·COMe} \\ \text{NPh——CO}\end{array}$$
(III.)


$$\begin{array}{l}\text{N:CMe·CH·CMe}_2\text{·CH}_2 \\ \text{NPh——C═CH——CO}\end{array}$$
(IV.)

(V.)

$$\begin{array}{l}\text{N:CMe·CH·CHPh·CH}_2\text{·COMe} \\ \text{NPh——CO}\end{array}$$

compound, *e.g.*, benzylidene-1-phenyl-3-methylpyrazolone, is first formed. Also in certain cases the indogenide intermediate product is formed, and 1-phenyl-3-methylpyrazolone should add on to other substances with unsymmetrical heterogeneous conjugated systems. With mesityl oxide and styryl methyl ketone, it forms the *compounds* $C_{16}H_{20}O_2N_2$ (III), m. p. 142—144°, with some (IV), m. p. 117°, and $C_{20}H_{20}O_2N_2$ (V), m. p. 161—162°.

A. A. ELDRIDGE.

Behaviour of pyrazine compounds. I. C. GASTALDI and E. PRINCIVALLE (Gazzetta, 1928, 58, 412—416).—The Rung–Behrend–Pinner reaction for glyoxalines is also given by pyrazines; the compound described by Pinner (A., 1905, i, 476) as 2-benzoyl-5-phenylglyoxaline, and by Gastaldi (A., 1921, i, 605) as 6-hydroxy-2 : 5-diphenylpyrazine, by methylation yields 2 : 5-diphenyl-1-methyl-6-keto-1 : 6-dihydropyrazine-4-methiodide, which when treated with potassium hydroxide loses methylamine. Similarly, 6-hydroxy-2 : 5-dimethylpyrazine (Gastaldi, *loc. cit.*) yields 1 : 2 : 5-*trimethyl*-6-*keto*-1 : 6-*dihydropyrazine*-4-*methiodide*, which also loses methylamine.

3 : 6-Dicyano-2 : 5-dimethylpyrazine (*loc. cit.*) is hydrolysed by sulphuric acid to the *diamide*, m. p. 290°, of 2 : 5-dimethylpyrazine-3 : 6-dicarboxylic acid, m. p. 194—195° (Wleügel, A., 1882, 949, gives 200°, but the observed value, 85—86°, for the m. p. of the ethyl ester).

E. W. WIGNALL.

Steric hindrance in reactions of substituted quinoxalines. G. M. BENNETT and G. H. WILLIS (J.C.S., 1928, 1960—1975).—A comparative study was made of the condensation of 2- and 2 : 3-substituted methyl and benzyl derivatives of quinoxaline with aromatic aldehydes and their reaction with bromine. The reactivity of 2 : 3-dimethylquinoxaline is of the same order as that of 2-methylquinoline, and is attributed to general and alternating polar influences. The polarisation may conceivably lead to tautomeric change, and it is pointed out that the possibility of such a change is a general accompaniment of reactivity of methyl groups. The usual products of condensation of 2 : 3-dimethylquinoxaline with aldehydes were distyrylquinoxalines, but monostyrylquinoxalines were isolated as well from *p*-methoxy- and *m*-nitro-benzaldehydes, and *o*-methoxybenzaldehyde yielded solely the monostyryl derivative. Nitrobenzaldehydes, particularly the *p*- and 2 : 4-derivatives, reacted readily, but methoxybenzaldehydes more slowly. It is suggested that these facts may be explained as an effect of steric hindrance due to the configuration of the monostyrylquinoxaline which is determined by the polarity of the groups present. Thus sufficient attraction exists between the nitrogen atoms of quinoxaline and nitro-groups for an additive *compound*, $C_{10}H_{10}N_2,2C_6H_3(NO_2)_2CHO$, m. p. 96—97°, to be formed from 2 : 3-dimethylquinoxaline and 2 : 4-dinitrobenzaldehyde. In a mono-*o*-nitrostyryl derivative the attraction between the quinoxaline nitrogen atom and the nitro-group will impose a configuration which leaves the second quinoxaline methyl group free, but the repulsion in the case of a mono-*o*-methoxystyryl derivative will impose a spatial arrangement which hinders reaction of the second methyl group. That pure steric hindrance is not the only factor is shown by the ready formation of a distyryl derivative with *o*-iodobenzaldehyde. The 6-methyl group in 2 : 3 : 6-trimethylquinoxaline is not reactive, but increases the reactivity of the 2- and 3-groups. None of the 2-phenyl-3-benzylquinoxalines prepared showed any reactivity of the methylene of the benzyl group, owing to the steric hindrance of the two phenyl groups.

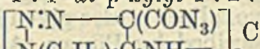
2-*Benzylquinoxaline*, an oil (*picrate*, m. p. 117°), was prepared from benzylglyoxal and *o*-phenylenediamine. *Phenyl* β-*methoxy*-p-*chlorostyryl ketone*, b. p. 238°/16 mm., m. p. 45°, prepared from ω-methoxyacetophenone by condensation with *p*-chlorobenzaldehyde, was converted into *phenyl* p-*chlorobenzyl diketone*, m. p. 85°, by the action of hydrobromic acid, and 2-p-*chlorobenzyl*-3-*phenylquinoxaline*, m. p. 142°, was prepared by condensation with *o*-phenylenediamine. Hydrolysis of *phenyl* β : 3-*dimethoxystyryl ketone*, b. p. 245°/18 mm., yielded a *substance*, m. p. 175—180° (decomp.), which did not react with *o*-phenylenediamine.

Condensation with aldehydes was generally carried out in boiling acetic anhydride. The yield in each case was determined. The following substituted *quinoxalines* were prepared: 2-(2 : 4-*dinitrostyryl*)-, m. p. 219—220° (decomp.); 2-o-*nitrostyryl*-, m. p. 156°; 2-m-*nitrostyryl*-, m. p. 199·5°; 2-p-*nitrostyryl*-, m. p. 200°; 2 : 3-*distyryl*-, m. p. 190·5° (*tetrabromide*, m. p. 190°); 2-*methylenedioxystyryl*-3-*methyl*-, m. p. 150°; 2 : 3-*di*(*methylenedioxystyryl*)-, m. p. 208°; 2-m-*nitrostyryl*-3-*methyl*-, m. p. 184°; 2 : 3-*di*-(m-*nitrostyryl*)-, m. p. 237°; 2-p-*methoxystyryl*-3-*methyl*-, m. p. 122·5°; 2 : 3-*di*-(p-*methoxystyryl*)-, m. p. 163°; 2 : 3-*di*-(m-*methoxystyryl*)-, m. p. 126°; 2-o-*methoxystyryl*-3-*methyl*-, m. p. 112°; 2 : 3-*di*-(3 : 4-*dimethoxystyryl*)-, m. p. 208°; 2 : 3-*di*-(β-*furylvinyl*)-, m. p. 169°; 2 : 3-*di*-(o-*nitrostyryl*)-, m. p. 194·5°; 2 : 3-*di*-(p-*nitrostyryl*)-, m. p. 288°; 2-(2 : 4-*dinitrostyryl*)-3-*methyl*-, m. p. 224—225° (decomp.); 2 : 3-*di*-(2 : 4-*dinitrostyryl*)-, m. p. 295—297° (decomp.); 2-(2 : 4 : 6-*trinitrostyryl*)-3-*methyl*-, m. p. 250—251° (decomp.); 2 : 3-*di*-(o-*chlorostyryl*)-, m. p. 189·5°; 2 : 3-*di*-(m-*chlorostyryl*)-, m. p. 149°; 2 : 3-*di*-(p-*chlorostyryl*)-, m. p. 218°; 2 : 3-*di*(o-*iodostyryl*)-, m. p. 179°; 2 : 3-*distyryl*-6-*methyl*-, m. p. 193°; 2 : 3-*di*-(*methylenedioxystyryl*)-6-*methyl*-, m. p. 168°; 2-p-*methoxystyryl*-3 : 6-*dimethyl*-, m. p. 116°; 2 : 3-*di*-(p-*methoxystyryl*)-6-*methyl*-, m. p. 136°; 2 : 3-*di*-(3 : 4-*dimethoxystyryl*)-6-*methyl*-, m. p. 205°; 2-m-*nitrostyryl*-3 : 6-*dimethyl*-, m. p. 165°; 2 : 3-*di*-(m-*nitrostyryl*)-6-*methyl*-, m. p. 244·5°; 2 : 3-*di*-(2 : 4-*dinitrostyryl*)-6-*methyl*-, m. p. 251—255° (decomp.); 2-*styryl*-3-*phenyl*-, m. p. 149°; 2-p-*nitrostyryl*-3-*phenyl*-, m. p. 233°; 2-(2 : 4-*dinitrostyryl*)-3-*phenyl*-, m. p. 215°; 2-(β-*phenyl*-p-*nitrostyryl*)-, m. p. 149°; 2-(β-*phenyl*-2 : 4-*dinitrostyryl*)-, m. p. 261—262°. Quinoxalino*cyclo*pentane yielded a *dibenzylidene* derivative, m. p. 213°, and a *di*-p-*nitrobenzylidene* derivative, decomp. 268—270°. By the condensation of quinoline bases with 2 : 4-dinitrobenzaldehyde, 2-(2 : 4-*dinitrostyryl*)*quinoline*, m. p. 200°, and the 8-*methyl*, m. p. 198°, and 3-*methyl* derivative, m. p. 257°, were obtained. 2 : 3-Dimethylquinoline and benzaldehyde yielded 2-*styryl*-3-*methylquinoline*, m. p. 102°. Condensation of 2 : 3-dimethylquinoxaline with ethyl oxalate, preferably with potassium ethoxide, yielded *ethyl* 2-*methylquinoxaline*-3-*pyruvate*, m. p. 129° (p-*nitrophenylhydrazone*, m. p. 189°).

Bromination of the quinoxalines was carried out at 100° in acetic acid with bromine and acetic acid. 2-Methylquinoxaline yielded 2-ω-tribromomethylquinoxaline, m. p. 109°. In other cases steric hindrance supervened, 2 : 3-dimethylquinoxaline yielding only 2 : 3-*di*-(ω-*dibromomethyl*)*quinoxaline*, m. p. 228°, the symmetrical structure of which was shown by its hydrolysis by silver acetate to an unstable dialdehyde. 3-*Phenyl*-2-ω-*dibromomethylquinoxaline*, m. p. 148°, was similarly prepared. Phenylbenzyl- and phenyl-*p*-chlorobenzyl-quinoxalines yielded acetoxy-compounds, in which the reactive bromine of the intermediate monobromo-compound had reacted with the sodium acetate. 3-*Phenyl*-2-*phenylacetoxymethylquinoxaline*, m. p. 126°, and 3-*phenyl*-2-p-*chlorophenylacetoxymethylquinoxaline*, m. p. 119°, were obtained. 3-Phenyl-2-*p*-methoxybenzylquinoxaline did not react.

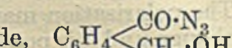
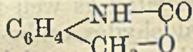
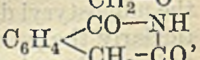
2 : 3-*Dimethylquinoxaline monomethiodide*, m. p. 192°, was prepared by heating the base with large excess of methyl iodide. It condensed with benzaldehyde or *p*-nitrosodimethylaniline to give black, insoluble products. 2 : 3-Dimethylquinoxaline did not react with amyl nitrite, Michler's hydrol, *p*-nitrosodimethylaniline, or a 2 : 4-dinitrobenzenediazonium salt. R. K. CALLOW.

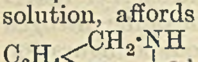
1 : 2 : 3-Triazoles. I. Reaction of aryl azides with hot alcoholic sodium alkoxides. A. BERTHO and F. HOLDER (J. pr. Chem., 1928, [ii], **119**, 173—188; cf. Bertho, A., 1925, i, 840).—The formation of 1-aryl-1 : 2 : 3-triazoles by heating aryl azides with an alcohol and the corresponding sodium alkoxide proceeds according to the equations (i) $CH_2R{\cdot}CH_2{\cdot}ONa=CHR{:}CH{\cdot}ONa+H_2$; (ii) $ArN_3+H_2=ArNH_2+N_2$; (iii) $ArN_3+CHR{:}CH{\cdot}ONa=(1)Ar{\cdot}C_2HN_3{\cdot}R(4)+NaOH$. It therefore depends on the ease of removal of hydrogen from the alkoxide, and hence ultimately on the "valency-need" of the group R, which occupies the 4-position in the resulting triazole. The yields of 4-substituted 1-*p*-xylyltriazoles, where R=Et, Pr^{β}, Me, Ph, are, respectively, 3, 2·5, 10, and 26%, and these figures are in accordance with the valency-need of these groups (Meerwein, A., 1920, i, 2). *p*-Xylyl azide, b. p. 90°/15 mm., reacts with sodium propoxide at 108° to give 1-p-*xylyl*-4-*methyl*-1 : 2 : 3-*triazole*, m. p. 57·5°, b. p. 165—170°; with sodium *iso*amyloxide at 130°, to give 1-p-*xylyl*-4-iso*propyl*-1 : 2 : 3-*triazole*, m. p. 118°; with sodium β-phenylethoxide at 120° to give 4-*phenyl*-1-p-*xylyl*-1 : 2 : 3-*triazole*, m. p. 129°. Sodium ethoxide and *n*-butoxide yield no isolable triazoles, and by prolonged action only *p*-xylenol. The constitution of the by-product from phenyl azide and any sodium alkoxide (*loc. cit.*), m. p. 282° (decomp.) when pure, mol. wt. 122—129 (not reconcilable with analysis), remains unknown; no corresponding substance is obtained with *p*-xylyl azide. C. HOLLINS.

1 : 2 : 3-Triazoles. II. Behaviour of 1-*p*-xylyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid in the Curtius reaction. A. BERTHO and F. HOLDER (J. pr. Chem., 1928, [ii], **119**, 189—198).—Methyl 1-*p*-xylyl-1 : 2 : 3-triazole-4 : 5-dicarboxylate (Michael, Lühn, and Higbee, A., 1898, i, 495), m. p. 86° [free acid, m. p. 151° (decomp.)], reacts with hydrazine hydrate in alcohol to give a normal *dihydrazide*, m. p. 133·5° (*acetone* compound, m. p. 207°; *dibenzylidene* derivative, m. p. 186°), together with a cyclic *monohydrazide*, m. p. 286° (*silver* salt described). The dihydrazide is converted by nitrous acid into 5-*carbimido*-1-p-*xylyl*-1 : 2 : 3-*triazole*-4-*carboxylic azide*, decomp. 150°, which when boiled with absolute methyl alcohol yields, instead of the expected 4 : 5-diamine, 4 : 4′-*diazidocarbonyl*-1 : 1′-*di*-p-*xylyl*-1 : 2 : 3-*triazolyl*-5 : 5′-*carbamide*,  $\left[\begin{matrix}N{:}N\text{——}C(CON_3)\\ N(C_8H_9){\cdot}C{\cdot}NH\text{—}\end{matrix}\right]_2CO$, m. p. 164°. Boiling with absolute ethyl alcohol gives only resinous products. C. HOLLINS.

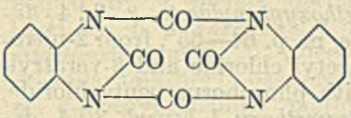
[Porphyrins and their syntheses.] H. FISCHER (Ber., 1928, **61**, [*B*], 1596).—A reply to Schumm (this vol., 776). H. WREN.

Degradation of *o*-substituted aromatic acid azides. H. LINDEMANN and W. SCHULTHEIS (Annalen, 1928, **464**, 237—253).—According to Stieglitz (A., 1914, i, 268), the thermal decomposition of azides gives, as a necessary intermediate, a free radical, R·CO·N⁚, but there is no experimental evidence for the existence of such compounds at any stage of the process. The thermal decomposition has now been effected of *o*-substituted aromatic acid azides, which, if they decomposed according to Stieglitz' view, should give one type of cyclic compound, but an entirely different one if intermediate carbimide formation took place. The conversion of *o*-hydroxybenzoyl azide into 2-hydroxyindoxazen and not into 1-hydroxybenz*iso*oxazole, reported previously (A., 1927, 262), is now regarded as evidence against the Stieglitz view, and the following facts point in the same direction.

o-Hydroxymethylbenzoyl azide,  $C_6H_4{<}\begin{matrix}CO{\cdot}N_3\\ CH_2{\cdot}OH\end{matrix}$, m. p. 74—75° (decomp.), which, contrary to the statement of Wedel (A., 1900, i, 363), is readily obtained from the corresponding hydrazide, passes, when melted or when heated in benzene solution, into 3-*keto*-3 : 4-*dihydro*-2 : 4-*benzoxazine*,  $C_6H_4{<}\begin{matrix}NH\text{—}CO\\ CH_2\text{—}O\end{matrix}$, and not into the isomeric compound,  $C_6H_4{<}\begin{matrix}CO\text{—}NH\\ CH_2\text{—}CO\end{matrix}$, which would result if a free radical were formed intermediately. The benzoxazine, m. p. 119—120°, is converted by boiling 50% sodium hydroxide into *o*-aminobenzyl alcohol.

Again, when the lactone of *o*-hydroxyphenylacetic acid is treated with alcoholic hydrazine hydrate it affords o-*hydroxyphenylacetylhydrazide*, m. p. 152°, normally convertible into o-*hydroxyphenylacetyl azide*, m. p. 51°. The latter, when heated in benzene solution, affords 2-*keto*-3 : 4-*dihydro*-1 : 3-*benzoxazine*,  $C_6H_4{<}\begin{matrix}CH_2{\cdot}NH\\ O\text{——}CO\end{matrix}$, m. p. 188°, converted by alkali and benzoyl chloride into ON-*dibenzoyl*-o-*hydroxybenzylamine*, m. p. 141·5°. The latter on partial hydrolysis affords N-*benzoyl*-o-*hydroxybenzylamine*, m. p. 144°.

Phthalyl diazide, from phthaloyl chloride and sodium azide in acetone solution, is highly explosive and cannot be manipulated at all readily. A less explosive *isomeride*, m. p. 56° (decomp.), is formed at the same time, and if the benzene solution of either is boiled, there results o-*carbimidobenzoyl azide*, $N_3CO\cdot C_6H_4\cdot NCO$, m. p. 60° (decomp.); at 100° the mass solidifies and melts again at 325°, when it consists of the *substance* (IV) (more readily obtained by boiling a freshly prepared toluene solution of phthalyl diazide), converted by boiling aniline into *s*-diphenylcarbamide, benzimazolone and *benziminazolone*-1-*carboxyanilide*, m. p. 197° (hydrolysed to benziminazolone by warm alkali).

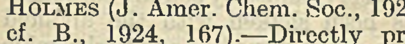

(IV.)

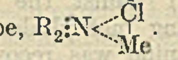
Either diazide, when kept in methyl-alcoholic solution, yields o-*carbomethoxyaminobenzoyl azide*, $N_3CO\cdot C_6H_4\cdot NH\cdot CO_2Me$, which melts at 80° (decomp.), the fused mass then becoming solid and finally melting at 155°, owing to its conversion into *methyl benziminazolone*-1-*carboxylate*, m. p. 159°. The latter is also obtained by boiling a toluene solution of the last-named azide. o-*Carbethoxyaminobenzoyl azide*, m. p. 64—66° (decomp.), similarly passes into *ethyl benziminazolone*-1-*carboxylate*, m. p. 156°. This ester and the methyl analogue are converted into benziminazolone when a solution of either in alkali is acidified.

When aniline is added to a benzene solution of o-carbimidobenzoyl azide, o-*phenylcarbimidobenzoyl azide*, $N_3CO\cdot C_6H_4\cdot NH\cdot CO\cdot NHPh$, m. p. 133°, is formed, the latter passing, in boiling toluene solution, into benziminazolone-1-carboxyanilide (above).

The more explosive and less explosive phthalyl diazides are possibly the symmetrical and unsymmetrical compounds, respectively, corresponding with the two phthalyl chlorides. E. E. TURNER.

Tautomerism of brilliant-cresyl-blue. W. C. HOLMES (J. Amer. Chem. Soc., 1928, **50**, 1989—1993; cf. B., 1924, 167).—Directly prepared chloroform solutions of this oxazine dye,


$NH_2\cdot C_6H_3<\overset{N}{\underset{O}{}}\!\!>C_6H_2Me{:}NMe_2Cl$, contain principally a blue tautomeride which is also present in dilute aqueous solutions. On saturating the solution with ammonia this is converted with loss of one methyl group into a brown dye-base, which readily regenerates a blue dye with acids. When, however, the dye is extracted with chloroform from a solution in a $0{\cdot}15M$-acetate buffer which is $0{\cdot}6N$ with regard to sodium chloride (p_H 3·42), the extract contains mainly a violet tautomeride which is also present in concentrated aqueous solutions. The absorption spectrum of the chloroform solution is only slightly altered by saturation with ammonia, most of the violet form remaining unattacked. Accordingly, the blue form is assigned the generally accepted formula (above), whilst the much less reactive violet form is represented as an additive product of the type,


$R_2{:}N\!<\!\overset{Cl}{\underset{Me}{|}}$.

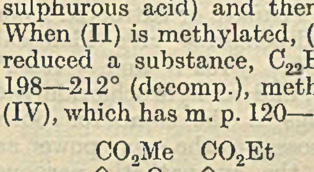
H. E. F. NOTTON.

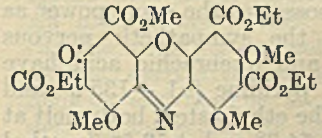
Action of diazomethane on ethyl phloroglucinoldicarboxylate and its derivatives; its reaction with nitrous acid. H. LEUCHS [with I. WALDORF, P. SANDER, and W. R. LEUCHS] (Annalen, 1928, **460**, 1—32).—Treatment of ethyl phloroglucinoldicarboxylate (cf. Annalen, 1924, **440**, 149), with benzoyl chloride in presence of light petroleum and ferric chloride gives the O-*benzoyl* derivative, m. p. 137—138°, converted by diazomethane into the *methyl*, m. p. varying between 102—103° and 116—118°, and *dimethyl ether*, m. p. 106°. The latter with cold alcoholic alkali gives the benzoyl-free *ester*, m. p. 146—147°, whilst the hot reagent produces the *dimethyl ether*, m. p. 186—188°, of the corresponding acid, converted by bromine in hydrobromic-acetic acid into the *compound*, $C_9H_9O_5Br$, m. p. 220° (decomp.). The ester, m. p. 146—147°, results when ethyl phloroglucinoldicarboxylate is treated with diazomethane.

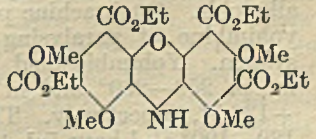
Phloroglucinoldicarboxylic acid trimethyl ether (decomp. 260°), from the corresponding ester, is converted by the above brominating mixture into dibromophloroglucinol trimethyl ether. The *bromo*-derivatives of the trimethyl ethers of phloroglucinoldicarboxylic acid and ester melt, respectively, at 165—173° (decomp.) and 51°.

Diazomethane converts the nitro-derivative (A., 1909, i, 106) of ethyl phloroglucinoldicarboxylate into the *trimethyl ether*, hydrolysed to the corresponding *acid*, m. p. 132—135° (*methyl* ester, m. p. 70—71°). *Nitrophloroglucinol trimethyl ether* has m. p. 151—152°. *Ethyl* 1 : 2 : 3 : 5-*tetramethoxybenzene*-4 : 6-*dicarboxylate* has m. p. 64—65°. *Ethyl* N-*dimethylaminophloroglucinoldicarboxylate* has m. p. 151—152°. *Phloroacetophenonedicarboxylic acid trimethyl ether* has m. p. 142—144° (sinters 138°) (*ethyl* ester, oily; *methyl* ester, m. p. 74°).

The compound, obtained from ethyl phloroglucinoldicarboxylate and nitric acid, previously regarded (*loc. cit.*) as $C_{22}H_{21}O_{13}N$, is now shown to be $C_{24}H_{23}O_{14}N$, and is called *ethyl phlorazurin*-1 : 3 : 6 : 8-*tetracarboxylate* (I). Diazomethane converts this into the *trimethyl ether*, m. p. 100—101°. When a solution of (I) in ethyl acetate is boiled for 1 day, the N:O group is reduced and one ester group is hydrolysed, giving the same substance, $C_{22}H_{19}O_{13}N$ (II), as is obtained when (I) is first reduced (by means of boiling alcohol, or by sulphurous acid) and then heated in ethyl acetate. When (II) is methylated, (III) results, and when it is reduced a substance, $C_{22}H_{21}O_{13}N$, is formed, m. p. 198—212° (decomp.), methylation of which produces (IV), which has m. p. 120—121°. The reduction of (I) with alcohol, referred to above, actually produces the corresponding *phenoxazone*, *i.e.*, the previously described compound, $C_{22}H_{21}O_{12}N$, the *trimethyl ether* of which has m. p. 112—113°. When the phenoxazone


(I.)

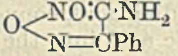

(III.)


(IV.)

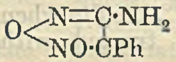
is heated with alcoholic hydroxylamine it gives two *oximes*, m. p. 141° and 138°, for which formulæ are proposed.

Other reactions of (I) and derived compounds are discussed. For these the original should be consulted. E. E. TURNER.

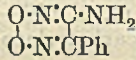
Dioximes. XLIX. A. VIANELLO (Gazzetta, 1928, **58**, 326—328; cf. Ponzio and Cerrina, this vol., 414).—When dissolved in 10% sulphuric acid and treated with bromine water, β-phenylaminoglyoxime decomposes with evolution of gas, but the α-compound yields *phenylaminoperoxide*,



$\mathrm{O}<\begin{matrix}\mathrm{NO{:}\overset{}{C}{\cdot}NH_2}\\ \mathrm{N{=}CPh}\end{matrix}$ or



$\mathrm{O}<\begin{matrix}\mathrm{N{=}C{\cdot}NH_2}\\ \mathrm{NO{\cdot}CPh}\end{matrix}$ or



$\begin{matrix}\mathrm{O{\cdot}N{:}C{\cdot}NH_2}\\ \mathrm{O{\cdot}N{:}CPh}\end{matrix}$, m. p. 142°, which is neither hydrogenated by zinc and acetic acid nor deoxygenated by stannous chloride, but is slowly converted into phenylaminofurazan by tin and hydrochloric acid. The two forms of *p*-tolylaminoglyoxime exhibit similar difference in their behaviour towards bromine water. p-*Tolylaminoperoxide*, $C_9H_9O_2N_3$, m. p. 178°, is reduced by tin and concentrated hydrochloric acid to p-*tolylaminofurazan*, $C_{13}H_{15}O_4N_3$, m. p. 142°, which is also obtained by treatment of *diacetyl-α-*p-*tolylaminoglyoxime*, m. p. 168°, with 20% sodium hydroxide solution.

T. H. POPE.

Synthesis of physostigmol ethyl ether. S. KEIMATSU and S. SUGANUMA (J. Pharm. Soc. Japan, 1928, No. 554, 348—355).—Physostigmol ethyl ether (Stedman, A., 1924, i, 981) is obtainable by the following method: *p*-Ethoxybenzenediazonium chloride and ethyl potassioacetoacetate give *ethyl β-methylpyruvate* p-*ethoxyphenylhydrazone*, m. p. 113—114°, which on boiling with 10% alcoholic sulphuric acid is converted into *ethyl 5-ethoxy-3-methylindole-2-carboxylate*, m. p. 168—169°. The corresponding *acid*, m. p. 183—184° (decomp.), loses carbon dioxide at 200° giving 5-ethoxy-3-methylindole (norphysostigmol ethyl ether), m. p. 65—66° (*picrate*, m. p. 113°), which, on treating with sodium and methyl iodide, gives 5-ethoxy-1 : 3-dimethylindole (physostigmol ethyl ether), m. p. 86°. K. ISHIMURA.

Identity of yohimbine and quebrachine. RAYMOND-HAMET (Compt. rend., 1928, **187**, 142—145).—Quebrachine obtained from the bark of *Aspidosperma Quebracho blanco* and yohimbine isolated from the bark of *Pausinystalia Yohimbe* or extracted from Gustrow's yohimbine hydrochloride give identical figures on analysis, have [α] +102·7° and +102·2° (in pyridine), respectively, and as hydrochloride the lethal dose for guinea-pigs is the same for both alkaloids. Quebrachine possesses the same power as yohimbine of paralysing the sympathetic nervous system. Yohimbic acid and quebrachic acid have m. p. 259—260° and in pyridine [α] +135·9° and +136·7°, respectively. The ethyl esters both melt at 189—190° and have [α] +54·3° and +53·5° (in ethyl alcohol); similarly, the propyl esters, m. p. 136—137°, have [α] +48·1° and +47·8° (in ethyl alcohol). Yohimbine and quebrachine are therefore regarded as identical (cf. A., 1926, 1263; 1927, 471; this vol., 432). R. BRIGHTMAN.

Aporphine alkaloids. III. Synthesis of corytuberine dimethyl ether. J. M. GULLAND and R. D. HAWORTH (J.C.S., 1928, 1834—1838).—The method previously described (this vol., 532, 781) was applied to the synthesis of 3 : 4 : 5 : 6-tetramethoxyaporphine, the *d*-form of which was identical in properties with corytuberine dimethyl ether (Gadamer, A., 1912, i, 46).

2′-*Nitro*-3′ : 4′-*dimethoxyphenylaceto*-β-3 : 4-*dimethoxyphenylethylamide*, m. p. 64—65°, from 2-nitro-3 : 4-dimethoxyphenylacetyl chloride and β-veratrylethylamine, yielded, with phosphorus pentachloride, 2′-*nitro*-6 : 7 : 3′ : 4′-*tetramethoxy*-1-*benzyl*-3 : 4-*dihydro*isoquinoline, m. p. 159—160° [*hydrochloride*, m. p. 227° (decomp.)]. Reduction of the *methiodide* of this base, m. p. 105—107° (+EtOH), decomp. 180—190°, with zinc dust and hydrochloric acid yielded 2′-*amino*-6 : 7 : 3′ : 4′-*tetramethoxy*-1-*benzyl*-2-*methyltetrahydro*isoquinoline (*dihydrochloride*, m. p. 188—190°), which could be diazotised and coupled with β-naphthol. Diazotisation in methyl alcohol and sulphuric acid and warming yielded 3 : 4 : 5 : 6-*tetramethoxyaporphine*, an oil (*hydrochloride*; *hydriodide*; *methiodide*, darkening at 220°, decomp. 248°). This *dl*-base yielded, with *d*-tartaric acid, l-*corytuberine dimethyl ether* d-*hydrogen tartrate*, m. p. 219—221° (decomp.), $[\alpha]_D$ −148·2° in water. The *d*-base was separated as the *l*-hydrogen tartrate. The properties of this, the reactions of the free *d*-base, and the properties of the methochloride, were in close agreement with those recorded by Gadamer (*loc. cit.*) for the base from natural sources. Carbethoxycorytuberine dimethyl ether also had properties identical with those of the compound from natural sources (Osada, A., 1925, i, 283). R. K. CALLOW.

Microchemical reactions of hyoscyamine. M. WAGENAAR (Pharm. Weekblad, 1928, **65**, 549—551).—The alkaloid sublimes when heated, forming droplets which can be caused to crystallise by sodium carbonate solution which has been shaken with the alkaloid itself or with atropine. The periodide and perbromide crystallise very readily, and are highly characteristic. The precipitates with gold chloride and picric acid, under suitable conditions, also crystallise well.

S. I. LEVY.

Lupin alkaloids. I. G. R. CLEMO and G. C. LEITCH (J.C.S., 1928, 1811—1820).—A review of the literature is given. *i*-Lupanine, $C_{15}H_{24}ON_2$, from *Lupinus termis*, was found to be a diacidic base, yielding with hydrogen chloride in ether a *dihydrochloride*, m. p. 185° (decomp.), which decomposed to give the monohydrochloride when heated under reduced pressure. On the other hand, only a *monomethiodide*, m. p. 262—263°, and a *monomethosulphate*, m. p. 188°, decomp. 275°, could be obtained. Three methods of degradation were attempted: (*a*) decomposition of the methiodide with alkali hydroxides, (*b*) reduction, and (*c*) oxidation.

(*a*) Whilst the methiodide was unchanged by boiling methyl-alcoholic potassium hydroxide, and lupanine was recovered when the methiodide was distilled with solid sodium hydroxide, distillation with a mixture of sodium and potassium hydroxides yielded a mixture of *α-methyl-lupanine*, m. p. 123°, insoluble in water [*hydrochloride*, m. p. 209° (decomp.)], and β-*methyl-lupanine*, a water-soluble oil [separated as the *methiodide*, m. p. 272° (decomp.)], with traces of simpler bases. These simpler bases formed the bulk of the distillate when fusion was carried out with potassium hydroxide alone. A fraction of b. p. 88—92°/1 mm., from which was obtained a *picrate*, $C_{18}H_{20}O_7N_4$ or $C_{17}H_{18}O_7N_4$, m. p. 130—131°, accompanied by a *picrate*, decomp. 225°, and a *base*, $C_{13}H_{22}N_2$, b. p. 127—132°/1 mm. (*picrate*, m. p. 137°; *dimethiodide*, m. p. 202°, decomp. 280°), were isolated. A similar mixture of bases was obtained by distillation of α-methyl-lupanine methiodide with potassium hydroxide, but vacuum distillation of the methylammonium hydroxide derived from it yielded a *base*, $C_{17}H_{30}O_2N_2$, b. p. 210—215°/1 mm., the formation of which was ascribed to a change from $-CH_2{>}NMe_2\cdot OH$ to $\begin{matrix}-CH_2OH\\ -NMe_2\end{matrix}$.

(*b*) Heating lupanine with red phosphorus and hydriodic acid at 220° yielded *deoxylupanine*, $C_{15}H_{26}N_2$, b. p. 145°/1 mm. (*dihydrochloride*; *monopicrate*, m. p. 135°; *dipicrate*, m. p. 206—207°; *methiodide*, m. p. 226°). A comparison of the properties of deoxylupanine with those of sparteine, isomeric with it, indicated partial structural similarity for the compounds, including probably the presence of the quinuclidine ring-system, which is unaffected by this method of reduction. Deoxylupanine in an ethereal solution containing sulphur in suspension yielded an orange precipitate with hydrogen sulphide. Oxidation of deoxylupanine yielded iso*lupanine*, m. p. 113° (*monoethiodide*, m. p. 208°).

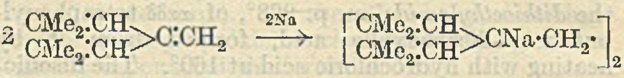
(*c*) Oxidation of lupanine with potassium permanganate in acetone yielded *oxylupanine*, b. p. 210°/1 mm., m. p. 123° [*chloroplatinate*, m. p. 232° (decomp.)], which had no reactive carbonyl, methylene, or hydroxyl group, or reactive tertiary nitrogen atom.

In the discussion of these results it is pointed out that the absence of carbonyl activity in any of the derivatives could be explained if they were α-quinuclidones, but the great stability to both acids and alkalis is against this hypothesis. R. K. Callow.

Salts of pelletierine. G. Tanret (J. Pharm. Chim., 1928, [viii], 8, 112—120).—Analyses of commercial samples of pelletierine sulphate and tannate show wide divergencies both in the character and amounts of total alkaloid present and many are complex mixtures containing little or no pelletierine. An example is given of two preparations containing tannates and sulphates of only ψ-pelletierine and *iso*pelletierine. The optimum conditions for the preparation of the tannates of pelletierine and ψ-pelletierine are described and the properties and methods for the analysis of the salts are given.

E. H. Sharples.

Alkali [metal]-organic compounds. W. Schlenk and E. Bergmann (Annalen, 1928, 463, 1—322; 464, 1—42).—The results described previously (A., 1914, i, 396) have been extended and are now subjected to systematic classification. **I. Products of addition of alkali metals to olefinic compounds.** The addition of sodium to olefinic compounds may occur in one or other of two ways: (I) represented by the case of tetraphenylethylene: $CPh_2{:}CPh_2 \longrightarrow CPh_2Na\cdot CPh_2Na$, or (II) represented by *as*-diphenylethylene: $2CPh_2{:}CH_2+2Na \longrightarrow CPh_2Na\cdot CH_2\cdot CH_2\cdot CPh_2Na$. In order that either addition may take place, an aryl group must in general be attached to the carbon atoms concerned in the ethylenic linkings, only one exception to this rule being known, viz. that in the scheme:



$$2\,\begin{matrix}CMe_2{:}CH\\ CMe_2{:}CH\end{matrix}{>}C{:}CH_2 \xrightarrow{2Na} \left[\begin{matrix}CMe_2{:}CH\\ CMe_2{:}CH\end{matrix}{>}CNa\cdot CH_2\cdot\right]_2$$

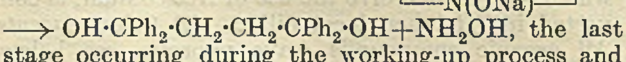
In some cases sodium can be added to an ethylenic linking present in a benzene nucleus. Thus 4-phenyldiphenyl affords a substance of the formula:

Lithium may also be added to olefinic compounds. In general, it adds more rapidly than sodium and sometimes leads to compounds having configurations different from those derived from the sodium compounds (see II below). Potassium is difficult to manipulate and is not likely to give results very different from those obtained with sodium.

The alkali-metal additive compounds have been systematically studied from the point of view of their behaviour towards certain reagents, as follows: (*a*) *Water.* This substance (or alcohol) effects replacement of sodium (or lithium) by hydrogen. (*b*) *Carbon dioxide.* With this reagent, $\cdot Na$ is replaced by $\cdot CO_2Na$. (*c*) *Alkyl iodides.* Methyl iodide converts a metal derivative formed by scheme I (above) into the original olefine (ethane formed), but one formed by scheme II into a saturated hydrocarbon in which methyl replaces sodium. (*d*) *Mercury.* This metal effects simple removal of sodium from compounds of an additive type, but does not affect compounds formed as a result of substitution of hydrogen by sodium. In a few cases mercury not only removes sodium, but also produces definite constitutional changes in the organic compound. This occurs with sodium compounds formed by scheme II. (*e*) *Thiocarbimides.* Compounds formed by scheme I undergo the reaction: $CR_2Na\cdot CR_2Na+2NR'{:}C{:}S \longrightarrow CR_2{:}CR_2+NR'Na\cdot CS\cdot CS\cdot NR'Na$, those formed by scheme II reacting analogously to the annexed process: $CPh_2Na\cdot CH_2\cdot CH_2\cdot CPh_2Na+2NEt{:}C{:}S \longrightarrow NEtNa\cdot CS\cdot CPh_2\cdot CH_2\cdot CH_2\cdot CPh_2\cdot CS\cdot NEtNa$, water converting the latter compound into $(NHEt\cdot CS\cdot CPh_2\cdot CH_2\cdot)_2$. (*f*) *Phenylcarbimide.* In general, the reagent undergoes conversion into its trimeride, no doubt owing to the action of traces of free sodium. Thus (cf. section V below) the sodium derivative of triphenylmethyl, the preparation of which does not involve the use of free sodium, is converted into triphenylacetanilide. (*g*) *Other reagents.* All organic compounds (save phorone, see below) capable of giving an enolic form behave towards the sodium derivatives as do water and alcohol (cf. Schlenk and Marcus, A., 1914, i, 823). Compounds derived by scheme I undergo this change simply, whilst those derived by scheme II behave more as Grignard reagents, the reaction being less rapid and sometimes more complicated.

[With H. Willstädt.]—Mercury converts disodiotetraphenylethane, from tetraphenylethylene, into the latter substance; disodio- or dilithio-dihydroanthracene into anthracene; and αδ-disodio-ααδδ-tetraphenylbutane into *as*-diphenylethylene. Disodiotetraphenylethane is converted by ethylthiocarbimide into the *disodium* derivative of dithiooxethylamide [see (*e*) above], whilst phenylthiocarbimide regenerates tetraphenylethylene. Ethylthiocarbimide converts disodiotetraphenylbutane into the *dithioethylamide*, m. p. 223°, of ααδδ-tetraphenylbutane-αδ-dicarboxylic acid, formed from it by heating with hydrochloric acid at 160°. The disodio-compound with phenylthiocarbimide gives a *substance*, $C_{50}H_{44}N_2S_3$(?), m. p. above 280°, and a second *substance*, m. p. 140°, whilst with phenylcarbimide the latter undergoes trimerisation. Further reactions of disodiotetraphenylethane are as follows (tetraphenylethylene being formed in addition to the substance mentioned): with bromobenzene, some diphenyl; with benzaldehyde, some benzyl alcohol; with furfuraldehyde, some furfuryl alcohol; with trioxymethylene, some sodium formate and some *ββγγ-tetraphenylbutane-αδ-diol*, m. p. 187°; with methyl benzoate some ethane (?); with phenyl benzoate, diphenyl (general reaction with benzoic and other esters which do not enolise: $2Ph{\cdot}CO_2R'+CR_2Na{\cdot}CR_2Na \longrightarrow CR_2{:}CR_2+2Ph{\cdot}CO_2Na+R{\cdot}R'$) (benzyl benzoate gives dibenzyl; methyl formate and ethyl oxalate obey the rule); with benzoyl chloride, benzil; with α-naphthoyl chloride *αα-naphthil*, m. p. 187° ($CR_2Na{\cdot}CR_2Na+R'{\cdot}COCl \longrightarrow CR_2{:}CR_2+NaCl+R'{\cdot}CNa{:}O$; $R'{\cdot}CNa{:}O+R'{\cdot}COCl \longrightarrow R'{\cdot}CO{\cdot}COR'$); with methyl chloroformate, methyl oxalate; with phorone, di*iso*butyl ketone. On the other hand, aniline converts disodiotetraphenylethane into tetraphenylethane and sodium-aniline, whilst ammonia is without action. Nitric oxide and the disodio-compound afford tetraphenylethane and sodium hyponitrite; carbon monoxide does not react, and sulphur dioxide produces tetraphenylethane and sodium tetraphenylethane-αβ-disulphinate.

Disodiotetraphenylbutane reacts as follows: Benzaldehyde gives *αββεεζ-hexaphenylhexane-αζ-diol*, m. p. 212° (sinters at 176°). Furfuraldehyde gives *ββεε-tetraphenyl-αζ-difurylhexane-αζ-diol*, m. p. 212—213°. Phenyl benzoate gives *αδ-dibenzoyl-ααδδ-tetraphenylbutane*, m. p. 195—196°. Benzoyl chloride gives 1 : 2 : 2 : 5 : 5-*pentaphenyl*cyclo*pentanol*, m. p. 179°, and its *benzoyl* derivative, m. p. 242°. Carbonyl chloride affords 2 : 2 : 5 : 5-*tetraphenyl*cyclo*pentanone*, m. p. 176°. Phorone gives tetraphenylbutane and the sodium derivative of enolic phorone. Nitrosyl chloride reacts according to the scheme, ⟶



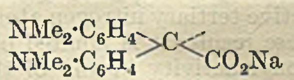
$$NO{\cdot}CPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2Na \longrightarrow \underbrace{CPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2}_{N(ONa)}$$

$\longrightarrow OH{\cdot}CPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2{\cdot}OH+NH_2OH$, the last stage occurring during the working-up process and thus affording ααδδ-tetraphenylbutane-αδ-diol.

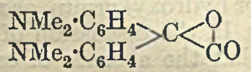
αα-Diphenyl-β-methyl-, αα-diphenyl-ββ-dimethyl-, α-phenyl-ββ-dimethyl-, β-phenyl-ααβ-trimethyl-, and αα-diphenyl-ββ-dibenzyl-ethylene do not combine with sodium, although they (see above) apparently have the necessary phenyl radical attached to an unsaturated carbon atom. These substances are therefore regarded as possessing formulæ other than those corresponding with the above names (see below). This view is supported by the fact that αα-diphenyl-β-benzylethylene, instead of combining with sodium, reacts with it (below) [compare the reaction of sodium with 1 : 2 : 3-triphenylindene (section III)], and is established as correct, since αα-diphenyl-ββ-dimethylethylene gives, with lithium, *γ-lithio-γγ-diphenyl-β-methylpropylene*, $CPh_2Li{\cdot}CMe{:}CH_2$ (below), the reactions of which prove its constitution. Since on the new view β-phenyl-ααβ-trimethylethylene is actually βγγ-triphenylpropylene, the conversion of this substance into ααβ-tribromo-β-bromomethylethylene (γ-bromo-ααβ-triphenylpropylene) by bromine is more readily understood than on Meisenheimer's view (A., 1927, 957). The only discordant result is that with ααβ-triphenyl-β-methylethylene, which gives the disodio-derivative, $CPh_2Na{\cdot}CPhMeNa$. This apparent anomaly is explained by assuming that there is first formed the radical $CHPh_2{\cdot}CPhNa{\cdot}CH_2{\cdot}$, which changes into ${\cdot}CPh_2{\cdot}CPhMeNa$, the latter then combining with an atom of sodium.

Nitriles capable of the tautomeric change: $CH_2R{\cdot}C{:}N \rightleftharpoons CHR{:}C{:}NH$, behave towards sodium as if they possessed the second formula, and give ${\cdot}NNa$ derivatives. Aromatic nitriles usually polymerise or condense in presence of sodium, but triphenylacrylonitrile combines additively with 2 atoms of sodium.

4 : 4′ : 4″ : 4‴-Tetra(dimethylamino)tetraphenylethylene and sodium afford the *disodio*-derivative of the corresponding ethane, since the latter is obtained by treating the product with alcohol, and since carbon dioxide converts the product into 4 : 4′ : 4″ : 4‴-tetra(dimethylamino)tetraphenylsuccinic acid. The *sodium* salt of the latter gives a deep blue aqueous solution which becomes colourless on warming. The blue and colourless solutions are explained on the basis of the annexed formulæ (free radical is blue):



$$(NMe_2{\cdot}C_6H_4)_2C({\cdot})\text{—}CO_2Na$$



$$(NMe_2{\cdot}C_6H_4)_2C<\underset{CO}{\overset{O}{|}}$$

[With J. APPENRODT.]—Bis-4-diphenylyl ketone and magnesium methyl iodide give *bis-4-diphenylylmethylcarbinol*, $(C_6H_4Ph)_2CMe{\cdot}OH$, m. p. 147°, converted by acetic and sulphuric acids at 100° into as-*bis-4-diphenylylethylene*, m. p. 211°. The latter reacts with sodium, giving the αδ-*disodio*-derivative of ααδδ-tetra-4-diphenylylbutane. Mercury converts this into the original ethylene, alcohol gives *ααδδ-tetra-4-diphenylylbutane*, m. p. 236°, and carbon dioxide gives *ααα′α′-tetra-4-diphenylyladipic acid*, m. p. above 300°.

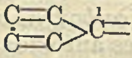
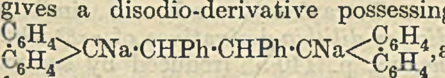
Triphenylethylene and sodium give the *disodio*-derivative of ααβ-triphenylethane (m. p. 56°, lit. 54°). Carbon dioxide converts the disodio-derivative into *triphenylsuccinic anhydride*, m. p. 115°. ααβ-Triphenyl-β-methylethylene (see above) adds sodium or lithium, the *products* being decomposed by alcohol to ααβ-triphenylpropane. αα-Diphenyl-β-methylethylene does not combine with sodium (above), whilst potassium slowly reacts to give a product which on one occasion gave with carbon dioxide a *substance*, $C_{17}H_{14}O_3$(?), m. p. 164°, and on another an *acid*, $(C_{16}H_{15}O_2)_n$, m. p. 259°.

Methyl *iso*butyrate and magnesium phenyl bromide give *diphenyl*iso*propylcarbinol*, m. p. 47°, b. p. 169—170°/12 mm., converted by way of the corresponding chloride (boiling pyridine) into αα-diphenyl-ββ-dimethylethylene, or, more probably, γγ-diphenyl-β-methylethylene, convertible into the above-described lithium compound, which with phenylthiocarbimide affords the *thioanilide*, m. p. 161°, of αα-diphenyl-β-methylvinylacetic acid. It is noted that Klages' supposed diphenyl-*n*-propylcarbinol (A., 1904, i, 487) is actually benzhydrol.

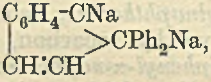
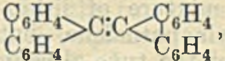
Interaction of ethyl dibenzylacetate and magnesium phenyl bromide produces *ααγ-triphenyl-β-benzylpropan-α-ol*, m. p. 100°, converted by way of the chloride into *αα-diphenyl-ββ-dibenzylethylene*, m. p. 78°, now regarded as *αγγ-triphenyl-β-benzylpropylene* (see above). β-Phenylpropionyl chloride and the Grignard reagent give *diphenyl-β-phenylethylcarbinol*, m. p. 87°, converted by acetic and sulphuric acids into *αα-diphenyl-β-benzylethylene*, b. p. 222°/10 mm., now regarded as *αγγ-triphenylpropylene*, slowly reacting with sodium to give a product affording the original hydrocarbon when decomposed with alcohol, and therefore probably possessing the formula $CPh_2Na{\cdot}CH{:}CHPh$.

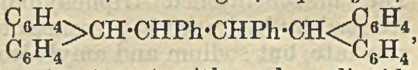
Sodium reacts very slowly with ααγγ-tetraphenylpropylene, to give products of an indefinite nature, but lithium in a reasonable time affords a product which, when decomposed with alcohol, gives 1 : 2 : 3-*triphenylhydrindene*, m. p. 153°. No explanation of this result appears possible. The lithium compound reacts with carbon dioxide to give 1 : 2 : 3-*triphenylhydrindenecarboxylic acid*, m. p. 275°, which when heated with soda-lime affords a *stereoisomeride*, m. p. 126°, of 1 : 2 : 3-triphenylhydrindene. That the lithium compound is a monosubstitution product and not an additive compound is shown by the formation of the above acid, and from its conversion by ethylthiocarbimide into a *compound*, $C_{30}H_{27}NS$, m. p. 193° (transparent at 173°). With iodine the lithium compound gives diphenylmethane, ααδδ-tetraphenylbutadiene, and a (trace) third *substance*, m. p. 221°.

Triphenylacrylonitrile and sodium afford the *disodio*-derivative of αββ-triphenylpropionitrile. Benzonitrile gives, besides its trimeride (cyaphenine), a *substance* isolated as the *perchlorate*, $C_7H_7N,HClO_4$.

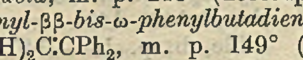
In fulvenes and diagrammatically similar compounds  $\begin{matrix}C{=}C\\ C{=}C\end{matrix}{>}\overset{1}{C}{=}\overset{2}{C}$, C_1 shows an exceptional tendency to combine with alkali metal. An example of a diagrammatically and chemically similar compound is the triolefine mentioned in the first paragraph above. The properties of C_2 depend largely on the nature of the groups attached to it. If it carries two aryl groups, it combines with sodium, but if it carries only one aryl group or alkyl groups, it reacts according to scheme II above. Thus benzylidenefluorene gives a disodio-derivative possessing the formula  $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}CNa{\cdot}CHPh{\cdot}CHPh{\cdot}CNa{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}$, a rather striking fact in view of the behaviour of stilbene and triphenylethylene. Another important fact is that compounds containing more than one ethylenic linking seldom combine with more than two atoms of sodium. Addition of sodium to one centre of unsaturation therefore appears largely to destroy the unsaturated properties of other such centres (cf. Ziegler, A., 1924, i, 308). Two exceptional cases are those of 9 : 9′-dianthryl and 10 : 10′-diphenyl-9 : 9′-dianthryl, which each combine with 4 at. of sodium.

Diphenylfulvene (1-diphenylmethylene*cyclo*pentadiene) readily affords the *disodio*-compound $C_4H_4{:}CNa{\cdot}CPh_2Na$, for alcohol converts the product into 1-*diphenylmethyl*cyclo*pentadiene* (1-*benzhydryl*cyclo*pentadiene*), $C_4H_4{:}CH{\cdot}CHPh_2$, m. p. 36·5°, whilst carbon dioxide produces the *dicarboxylic acid*, m. p. 173—175° (decomp.). On the other hand, dimethylfulvene (1-*iso*propylidene*cyclo*pentadiene) gives a *disodio*-compound of the formula $C_4H_4{:}CNa{\cdot}CMe_2{\cdot}CMe_2{\cdot}CNa{:}C_4H_4$, converted by carbon dioxide into an acid isolated as the *methyl* ester, $[C_4H_4{:}C(CO_2Me){\cdot}CMe_2{\cdot}]_2$, m. p. 194° (yield poor, owing to polymerisation, in first stage, produced by sodium).

1-Diphenylmethyleneindene affords the *disodio*-derivative,  $\begin{matrix}C_6H_4{-}CNa\\ |\\ CH{:}CH\end{matrix}{>}CPh_2Na$, converted by alcohol into 3-benzhydrylindene, m. p. 114° (Courtot, A., 1915, i, 392), isomerisation occurring during hydrolysis, since treatment of the disodio-compound with carbon dioxide affords 1-*benzhydrylindene*-ω-1-*dicarboxylic acid*, m. p. 177° (decomp.). 1-*iso*Propylideneindene polymerises in presence of sodium, and does not combine with it. 4 : 4′-Bisdiphenylylene–ethylene,  $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}C{:}C{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}$, gives the *disodio*-derivative of the corresponding ethane (m. p. 241—242°) [*dicarboxylic acid*, m. p. 240° (decomp.)]. Lithium gives similar results.

[With W. Schmidt-Nickels.]—Benzylidenefluorene reacts according to scheme II, the *disodio*-compound on decomposition (alcohol) affording *αβ-diphenyl-αβ-difluorenylethane*,  $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}CH{\cdot}CHPh{\cdot}CHPh{\cdot}CH{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}$, m. p. 321°, and on treatment with carbon dioxide giving *ββ′-diphenyl-ααα′α′-bisdiphenylyleneadipic acid*, decomp. 240°.

[With E. Müller.]—Furfurylidenefluorene behaves similarly, giving the *disodio*-derivative of *αβ-difuryl-αβ-difluorenylethane*, m. p. 238—242°. Cinnamylidenefluorene similarly affords the *disodio*-derivative of *αβ-difluorenyl-αβ-distyrenylethane*, m. p. 254—255°, together with a small amount of an *isomeride* (?), m. p. 204°. The latter compound is probably identical with a substance obtained by Thiele and Henle (A., 1906, i, 571); the other compound, m. p. 160—161°, obtained by reducing cinnamylidenefluorene, is probably a stereoisomeride of the above difluorenyldistyrenylethane.

Dixanthylene,  $O{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}C{:}C{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}O$, gives the *disodio*-derivative of dixanthyl, m. p. 209° (lit. 204—205°), the derived *dicarboxylic acid* having m. p. 189° (decomp.).

αα-Diphenyl-ββ-distyrenylethylene, $(CHPh{:}CH)_2C{:}CPh_2$, reacts rapidly with sodium, the product on decomposition giving *αβ-diphenyl-ββ-distyrenylethane*, m. p. 151—152°, or with carbon dioxide the *dicarboxylic acid*, m. p. 215° (decomp.), of the latter. *αα-Diphenyl-ββ-bis-ω-phenylbutadienylethylene*, $(CHPh{:}CH{\cdot}CH{:}CH)_2C{:}CPh_2$, m. p. 149° (from azibenzil and dicinnamylideneacetone), gives the *disodio*-derivative of *αα-diphenyl-ββ-bis-ω-phenylbuta-*

dienylethane, m. p. 140°. The expected *dicarboxylic acid* has m. p. 127° (decomp.).

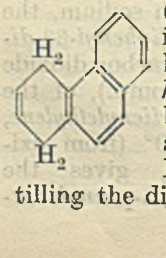
βζ-Dimethyl-δ-methylene-$\Delta^{\beta\epsilon}$-heptadiene is exceedingly readily converted by sodium into the *disodio*-derivative of βι-*dimethyl*-δη-*bis*-ω-*dimethylvinyl*-$\Delta^{\beta\theta}$-*decadiene*, b. p. 195—196°/58 mm. The δη-*dicarboxylic acid* of the latter results normally.

[With I. Rodloff.]—Tolane, which is most conveniently obtained by treating benzildihydrazone with mercuric oxide, gives ambiguous results with sodium, a *substance* (?), m. p. 295°, being the only product of the subsequent decomposition. On the other hand, lithium reacts fairly easily, and in a novel manner. It causes the combination of two molecules of tolane to give 1 : 2 : 3-*triphenylnaphthalene*, m. p. 151°, which reacts in two ways with the metal : (1) to give 4-*lithio*-1 : 2 : 3-*triphenylnaphthalene*, converted by alcohol into the above hydrocarbon, by carbon dioxide into 2 : 3 : 4-*triphenyl*-α-*naphthoic acid*, m. p. 258° (decomp.), and by phenylthiocarbimide into the *thioanilide*, m. p. 280—281°, of this acid, and (2) to give 1 : 2-*dilithio*-1 : 2 : 3-*triphenyl*-1 : 2-*dihydronaphthalene*, the presence of which is shown by the formation, in the above reaction with carbon dioxide, of the *anhydride*, m. p. 270°, of 1 : 2 : 3-*triphenyl*-1 : 2-*dihydronaphthalene*-1:2-*dicarboxylic acid* (not isolated). Mercury does not convert the mixture of lithio-derivatives into 1 : 2 : 3-triphenylnaphthalene, but into a *stereoisomeride*, $C_{28}H_{20}$ (? of the type already known in the diphenyl series), m. p. 227°, more readily produced by the action of iodine on the metal derivative. In one case where lithium and tolane remained together for several years, a third *isomeride*, $C_{28}H_{20}$, m. p. 192°, of the above hydrocarbon was obtained. The first-mentioned triphenylnaphthalene is not reduced by hydrogen in presence of palladised barium sulphate, but sodium and amyl alcohol afford a *hydrocarbon*, $C_{28}H_{24}$(?), m. p. about 75°.

[With O. Blum.]—When αα-dichloro- or αα-dibromo-ββ-diphenylethylene is treated with lithium and the product with alcohol, the triphenylnaphthalene, m. p. 152°, is formed. This when treated with lithium, with subsequent hydrolysis, gives the isomeride, m. p. 192°. Under different conditions the dihalogeno-compounds are converted by lithium into a *hydrocarbon*, $C_{28}H_{22}$, m. p. 184°, which when reduced catalytically, or when treated with lithium, followed by alcohol, is converted into a *hydrocarbon*, $C_{28}H_{24}$, m. p. 182°. The formation of triphenylnaphthalene is no doubt due to the intermediate formation of tolane.

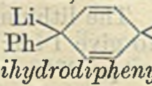
4 : 4′-Dimethoxytolane (prepared by oxidising *anisildihydrazone*, m. p. 118°) reacts extremely slowly with lithium, whilst diphenyldiacetylene is mainly polymerised by the latter.

Phenanthrene does not combine with lithium in the 9 : 10-positions, but in the 1 : 4-positions. The 1 : 4-*dihydrophenanthrene*, b. p. 168—170°/15 mm. (annexed formula) obtained (alcohol), is converted by hydrogen and palladised barium sulphate into 1 : 2 : 3 : 4-*tetrahydrophenanthrene*, and an *isomeride*, b. p. 140—149° (two fractions obtainable, b. p. 140—145° and 145—149°). From the residue obtained after distilling the dihydrophenanthrene, an *isomeride*, m. p. 71—73°, is obtained. Sodium reacts sluggishly with phenanthrene, the product being converted by carbon dioxide into 9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*diphenanthryl*-10 : 10′-*dicarboxylic acid*, m. p. 226° (cf. scheme II, above).



9 : 10-Diphenylphenanthrene combines with sodium or with lithium in the 9 : 10-positions. The so-obtained (alcohol) 9 : 10-*diphenyl*-9 : 10-*dihydrophenanthrene* has m. p. 130—131°, and the corresponding 9 : 10-*dicarboxylic anhydride* has m. p. 221°.

Ordinary naphthalene contains sufficient sulphur compounds to cause hindering of alkali-metal reactions, whilst Kahlbaum's "calorimetric" naphthalene, although reacting poorly with sodium for the same reason, is converted by lithium into 1 : 4-*dilithio*-1 : 4-*dihydronaphthalene* (identified by conversion into 1 : 4-dihydronaphthalene) and a lithium derivative of a *liquid*, b. p. 265—275°/14 mm. 1 : 4-*Dihydronaphthalene*-1 : 4-*dicarboxylic acid*, obtained normally, has m. p. 226—227°. Insufficiently long treatment of naphthalene with lithium gives rise, after alcohol treatment, to the known additive compound, m. p. 43—44°, of naphthalene and 1 : 4-dihydronaphthalene.

Diphenyl does not combine with sodium under the usual conditions, but lithium affords a dilithio-derivative, , which with alcohol produces 1:4-*dihydrodiphenyl*, b. p. 110°/10 mm., and with carbon dioxide gives 1 : 4-*dihydrodiphenyl*-1 : 4-*dicarboxylic acid*, m. p. 266° (276° ?) (decomp.). That addition occurs 1 : 4 is shown by the reduction of the dihydrodiphenyl to phenyl*cyclo*hexane, and by the impossibility of obtaining the dicarboxylic anhydride using acetic anhydride.

[With E. Müller.]—4-Phenyldiphenyl combines with sodium slowly in ether, but more rapidly in dioxan, giving a product converted by carbon dioxide into 1 : 4-*diphenyl*-$\Delta^{2:5}$-cyclo*hexadiene*-1 : 4-*dicarboxylic acid*, m. p. 264° (decomp.) (sinters 240°). 1 : 2 : 4 : 5-Tetraphenylbenzene and sodium, followed by alcohol, give 1 : 2 : 4 : 5-*tetraphenyl*-1 : 2-*dihydrobenzene* (2 : 3 : 5 : 6-*tetraphenyl*-$\Delta^{1:3}$-cyclo*hexadiene*). The *sodium* salt of the derived *dicarboxylic acid* [m. p. 230° (decomp.)] readily undergoes autoxidation.

II. New facts in the stereochemistry of carbon. [With J. Appenrodt.]—*trans*-*trans*-αδ-Diphenylbutadiene combines with sodium or lithium to give *dialkali* derivatives of αδ-*diphenyl*-Δ^{β}-*butene*, b. p. 176°/13 mm., *i.e.*, an ethylene isomeride of the known butene, m. p. 45°. With carbon dioxide they give αδ-*diphenyl*-Δ^{β}-*butene*-αδ-*dicarboxylic acid*, m. p. 220°, and are converted by mercury into the original butadiene. ααδδ-Tetraphenylbutadiene similarly gives the *disodio*- or *dilithio*-derivatives of ααδδ-*tetraphenyl*-Δ^{β}-*butene*, m. p. 140·5° (reduced by sodium and amyl alcohol to tetraphenylbutane, but not decolorising bromine). The αδ-*dicarboxylic acid*, m. p. 262° (decomp.), of the butene, and the corresponding *methyl* ester, m. p. 148—148·5°, are described. Methyl iodide or mercury converts the dialkali compounds into the butadiene. Reduction of the latter with sodium amalgam and alcohol gives the above butene, so that this case differs stereochemically from that of diphenylbutadiene.

[With E. Müller.]—*Mercury bis-ββ-diphenylvinyl*, $Hg(CH{:}CPh_2)_2$, m. p. 140·5°, from magnesium ββ-diphenylvinyl bromide and mercuric bromide (*mercury ββ-diphenylvinyl bromide* has m. p. 158—159°) reacts with sodium to give a disodio-derivative, which with carbon dioxide gives the dicarboxylic acid (m. p. 262°) of the above tetraphenylbutene, but with alcohol affords a *stereoisomeric* ααδδ-tetraphenyl-Δ^{β}-butene, m. p. 123—124°. The latter is converted into the butene, m. p. 140·5°, when warmed in glacial acetic acid in presence of a little sulphuric acid, and on reduction gives tetraphenylbutane. An explanation of these phenomena is put forward.

When addition of alkali metal to a poly-olefinic compound could theoretically give rise both to *cis-cis-* and to *cis-trans*-compounds, or to one of these, sodium and lithium may behave similarly or differently. Thus, when sodium (2 atoms) combines with stilbene, a meso-compound results, whilst lithium affords the corresponding *racemic* derivative. Assuming stilbene to possess the *cis-trans*-configuration, the sodium addition is *cis-trans*, the lithium *cis-cis*. The acid, m. p. 227°, previously obtained (1914, *loc. cit.*) from carbon dioxide and disodium stilbene, melts at 229—230° (decomp.) (*methyl* ester, m. p. 219°). The product of adding lithium to stilbene gives *s*-diphenylethane when treated with alcohol, and stilbene with mercury, whilst with carbon dioxide it gives a *diphenylsuccinic acid*, m. p. 241° (decomp.) (*methyl* ester, m. p. 169°, clearing at 191°). Addition of potassium to stilbene, followed by carbon dioxide treatment, gives the above meso-acid, m. p. 229—230° (decomp.) (cf. Wren and Still, J.C.S., 1915, 107, 444).

*iso*Stilbene, prepared by the catalytic reduction of tolane, is so rapidly converted by alkali metals into stilbene that the products obtained are the same as from the latter.

s-Diphenyldimethylethylene combines with sodium to give a disodio-compound which is converted by alcohol into the *s*-diphenyldimethylethane (βγ-diphenylbutane) obtained by catalytic hydrogenation of the olefine, and with carbon dioxide affords the same *s-diphenyldimethylsuccinic acid*, m. p. 296° (decomp.), as is similarly derived from the more readily obtained *dilithium* compound. The latter gives the ethylene when treated with mercury.

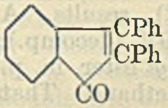
4-Benzoyldiphenyl (4-diphenylyl phenyl ketone) (preparation improved) is converted by phosphorus pentachloride into dichloro-4-diphenylylphenylmethane, $C_6H_5{\cdot}C_6H_4{\cdot}CPhCl_2$, m. p. 72° (lit. 45—47°), which, when heated in benzene solution with copper bronze, gives a mixture of the two, isomeric *s-diphenyl-bis-4-diphenylylethylenes*, m. p. 255° and 218°. Either isomeride combines with sodium or with lithium, the products of all four interactions giving, when treated with alcohol, two stereoisomeric *s-diphenylbis-4-diphenylylethanes*, m. p. 247° and 205—206°, respectively. This result is ascribed to the formation of a free radical (and consequent steric changes) during the decomposition with alcohol. The formation in all cases of the stabler of two isomerides in a mercury alkali-metal elimination is no doubt due to a similar cause.

4 : 4′-*Dimethoxyisostilbene*, obtained together with the corresponding ethane from the above tolane by catalytic reduction, has m. p. 37°. Distillation at 217—219°/14 mm. gives considerable dimethoxystilbene, also produced when the new compound is treated with lithium and then with mercury.

Wizinger (A., 1927, 764) regards the intense colour of sodium additive compounds of the type under discussion as being due to their co-ordinative structure. The disodio-derivatives of bisdiphenylylene-ethane and of αα-diphenyl-ββ-distyrenylethane (above) give electrical conductivities agreeing with this theory. That of the second (intensely coloured) is 20 times as great as that of the less highly coloured, first compound.

1 : 1 : 3-Triphenylindene is converted by sodium into a compound which, when decomposed with alcohol, affords a 1 : 1 : 3-*triphenylhydrindene*, m. p. 133°, whilst a *stereoisomeride*, m. p. 111—112°, of the latter results when the indene is reduced with hydrogen and palladised barium sulphate or with phosphorus and hydriodic and acetic acids. Both isomerides are colourless and that melting at 112° fuses to a colourless liquid; that melting at 133° affords a yellowish-green liquid on fusion.

The existence of two stereoisomeric triphenylhydrindenes can be explained only on the assumption that the two rings of indene and its derivatives are not co-planar, at any rate under some conditions of substitution. The optical resolution of 2 : 3-diphenylindone (annexed formula) establishes this as the correct explanation. When diphenylindone is treated with phosphorus pentachloride, it affords the 2 : 3-*dichloro*-2 : 3-*dihydro*-derivative, m. p. 135—136°. Aniline and the indone condense at the b. p. in presence of aniline hydrobromide to give 1-*anilo*-2 : 3-*diphenylindene*, m. p. 201° (sinters at 160°), whilst *d*-bornylamine condenses with benzophenone to give N-*diphenylmethylenebornylamine*, m. p. 170°, [α] +7·57°, and with diphenylindone to give a small quantity of N-*diphenylindenylidenebornylamine*, m. p. 123°, [α] +124°. This, after being hydrolysed, gives rise to a 2 : 3-diphenylindone phenylhydrazone having [α] −1·85°, which establishes the resolution during the purification of the bornylamine anil.

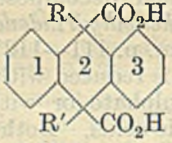


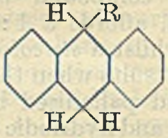
2 : 3-Diphenylindone, when catalytically reduced, gives 1-*hydroxy*-2 : 3-*diphenylhydrindene*, m. p. 146°, (the phenylcarbamate of which, when crystallised from anisole, undergoes thermal decomposition into diphenylindone and *s*-diphenylcarbamide), together with 2 : 3-*diphenyl*-1-*hydrindone*, m. p. 100°. The phenylhydrazone of 2 : 3-diphenylindone has m. p. 179—180°; lit. 175—176°.

[With W. Stoffers.]—When 3-phenyl-1-diphenylmethyleneindene is reduced with sodium and boiling amyl alcohol, 3-*phenyl*-1-*diphenylmethylhydrindene*, m. p. 137°, is formed, whilst when it is treated with sodium or lithium, followed by alcohol, there are formed 3-*phenyl*-1-*diphenylmethylindene*, m. p. 171° (giving the hydrindene, m. p. 137°, when reduced), and 1-*phenyl*-3-*diphenylmethylindene*, m. p. 131°. Sodium amalgam and alcohol convert 3-phenyl-1-diphenylmethyleneindene into the compound of m. p. 171°, together with an *isomeride*, m. p. 180°, which is very readily dehydrogenated. Indene-1-carboxylic acid is formed when indene is treated with lithium ethyl followed by carbon dioxide.

Other new cases of stereoisomerism have been discovered. Compounds having the structure (A), where R=R′=H or R=R′=Ph, exist in three forms, only to be accounted for if, with ring 2 in the plane of the paper, rings 1 and 3 are inclined towards the latter (the assumption that both inclinations are downwards is sufficient to explain the new facts; one downward and one upward inclination give an unlikely, and for the present, an unnecessary, configuration). Compounds of the structure (B) (R=Ph or CO_2H) exist in two forms, as do 9 : 9′-dianthranyl and 9 : 10-diphenylanthracene.

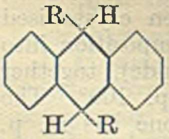
(A)



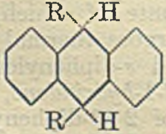


(B)

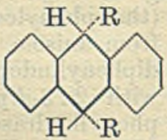
[With O. Blum and K. Ehninger.]—The 9 : 10-dihydroanthracene-9 : 10-dicarboxylic acid previously described (1914, *loc. cit.*) as melting at 287—288° (decomp.) has m. p. 286° (decomp.) and is now called the α-acid. The β-*acid*, m. p. 294° (decomp.; sinters 264°) or 283° (+$1H_2O$) (indef.), is obtained by a slight modification of the method of preparation of the α-acid from the product of adding sodium to anthracene. When lithium is used, a third (γ) *acid*, m. p. 297° (decomp.; sinters 267°), results. A mixture of β- and γ-acids melts at 297° (decomp.), and both acids give the same (β) *methyl* ester, m. p. 163·5—165°, when treated with diazomethane. That the β- and γ-acids are distinct is shown, however, by the fact that the γ-acid may be caused to form a hydrate. This loses all water of crystallisation when kept for 1 day, whilst the β-hydrate is stable. Moreover, salts of the β-acid readily pass into α-salts, whilst, for the conversion into the latter of γ-acid, prolonged boiling with excess of alkali is necessary. The β- and γ-acids show similar luminescence colours under cathode rays, the α-acid showing different colours. The ease of conversion of β into α and the difficulty of conversion of γ into α are explained if in the annexed scheme (outer rings inclined downwards) (R=CO_2H), the β-acid is A, and the γ-acid is B or C



(A)



(B)



(C)

(α-acid, C or B), since β ⟶ α involves one configurational change, whilst γ ⟶ α requires two.

Hydrolysis of the β-ester (above) gives neither β- nor γ-acid, but α-acid. Moreover, if instead of esterifying the α-acid with diazomethane (giving the α-*methyl* ester, m. p. 162·5—163°) boiling methyl-alcoholic hydrogen chloride is used, some β-ester is also formed. The latter is almost quantitatively produced when the pure α-ester is heated for 7 hrs. at 200°.

[With O. Blum.]—If 9 : 10-disodio-9 : 10-dihydroanthracene is treated in benzene solution with anthracene, 9-sodio-9 : 10-dihydroanthracene results, so that by the action of carbon dioxide 9 : 10-dihydroanthracene-9-carboxylic acid (α-acid), m. p. 207°, (not 208—210°, *loc. cit.*) (*methyl* ester, m. p. 94—96°) is obtained. If higher concentrations are used in the first stage, the β-dicarboxylic acid (above) is formed together with 9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthranyl*-10 : 10′-*dicarboxylic acid*, m. p. not below 370°, isolated as the *methyl* ester, m. p. 267°. Reduction of anthracene-9-carboxylic acid (catalytic) produces β-9 : 10-*dihydroanthracene*-9-*carboxylic acid*, m. p. 197° (sinters at 182°). Diazomethane converts the β-acid into the α-ester, m. p. 94—96°, which is also formed by the catalytic reduction of methyl anthracene-9-carboxylate. Three stereoisomeric 9 : 10-diphenyl-9 : 10-dihydroanthracene-9 : 10-dicarboxylic acids are obtained as follows: 9 : 10-Diphenylanthracene, prepared by heating 9-hydroxy-10-methoxy-9 : 10-diphenyl-9 : 10-dihydroanthracene (m. p. 244°, not 274° as lit.) with formic acid, is reduced by sodium and amyl alcohol to 9 : 10-diphenyl-9 : 10-dihydroanthracene, m. p. 208° (sinters at 180°; lit. m. p. 218°) (the "diphenyldihydroanthracene," m. p. 164·2°, described by Linebarger, 1891, has another constitution), and gives a *disodium* additive compound. The latter with alcohol gives a mixture of two (polymorphic) diphenyldihydroanthracenes, m. p. 199° and 190°, respectively, which are distinct from the compound, m. p. 208°, above. The latter slowly reacts with bromine to give a *tetrabromodiphenylanthracene*, $C_{26}H_{14}Br_4$, m. p. not below 300°, also formed, with great vigour, from either of the lower-melting compounds. Treatment of the above disodium compound with carbon dioxide, followed by addition of water and immediate acidification, gives the β-*acid*, m. p. 277°, whilst if the alkaline solution is heated (100°; ¼ hr.) before acidification, the α-*acid*, m. p. 299°, results. The γ-*acid*, m. p. 282°, is obtained from the *dilithio*-compound (alcohol converts this into the mixture of hydrocarbons obtained from the disodio-compound). All three acids, with diazomethane, give the same *methyl* ester, m. p. 201°.

No stereoisomeric 9-methyldihydroanthracene derivatives could be obtained, but 9-phenyl-9 : 10-dihydroanthracene exists in two forms. Reduction of 10-methoxy-10-phenylanthrone with phosphorus and hydriodic and acetic acids gives phenylanthrone, also obtained from phenylphthalide. The 9-phenylanthracene, obtained from the anthrone by reduction, is reduced by sodium and boiling amyl alcohol to α-9-phenyldihydroanthracene (obtained by Baeyer, 1880, but regarded by him as a more fully hydrogenated compound), m. p. 87°. The latter passes unchanged through the usual sodium, followed by alcohol, process. When the product of interaction of anthrone and magnesium phenyl bromide is decomposed with water, a 9-phenylanthracene is obtained, which when reduced with sodium and boiling amyl alcohol gives β-9-phenyldihydroanthracene, m. p. 123°, converted by the sodium–alcohol process into the α-compound, m. p. 87°. The latter does not react with sodium, which converts the β-compound into a *disodio*-derivative affording 9-phenylanthracene when treated with mercury.

9 : 9′-Dianthranyl, obtained by the method of Barnett and Matthews (J.C.S., 1923, **123**, 380), has m. p. 360° or higher, is reduced (sodium and amyl alcohol) to tetrahydro-9 : 9′-dianthranyl, m. p. 248—249°, and with sodium rapidly gives a product which gives indefinite results with carbon dioxide and is converted by alcohol into the latter hydrocarbon. When sodium diphenylmethyl, from benzhydryl methyl ether, reacts with 9-bromoanthracene, a second 9 : 9′-dianthranyl, m. p. 304°, results, its constitution following from its reduction (as above) to tetrahydrodianthranyl. It is clear, therefore, that the dianthranyl described by Liebermann and Gimbel in 1887 is an individual and not a mixture as stated by Barnett and Matthews (*loc. cit.*).

Two stereoisomeric 9 : 10-diphenylanthracenes are obtained as below: Phenylanthrone and magnesium phenyl bromide give 9-*hydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 202—203°, converted into the *methyl ether*, m. p. 226°, when treated with methyl iodide and potassium in xylene, but, when first heated with potassium and xylene and then treated with methyl iodide (ethyl iodide, or *iso*propyl, *tert.*-butyl, or benzyl chloride, or chloromethyl ether) affording the known (yellow) 9 : 10-diphenylanthracene, m. p. 247°, together with a colourless *isomeride*, m. p. 214°. Simultaneous interaction of sodium, methyl iodide, etc. gives only the yellow form. That the hydrocarbons are not simply dimorphic forms is established. Thus the compound, m. p. 247°, gives with sodium a product regenerating the original hydrocarbon when treated with mercury, whilst the hydrocarbon, m. p. 214°, similarly treated, is recovered unchanged. The two isomerides exhibit different colours in cathode rays. That they are not position isomerides is shown by their conversion by sodium and carbon dioxide into the same β-9 : 10-diphenyl-9 : 10-dihydroanthracene-9 : 10-dicarboxylic acid, and by lithium and carbon dioxide into the corresponding γ-acid. The sodium–mercury experiments appear to show that the isomerism is not that of *meso*- and *o*-quinonoid forms. Both forms give (free radicals?) yellow solutions in boiling ethyl benzoate.

Treatment of phenylanthrone with magnesium *o*-tolyl bromide gives 10-hydroxy-9-phenyl-10-*o*-tolyl-9 : 10-dihydroanthracene, m. p. 201°, which with potassium–*tert.*-butyl chloride–xylene gives a colourless *isomeride*, m. p. 172—173°, of the 9-*phenyl*-10-o-*tolylanthracene*, m. p. 257—258°, described below. 10-*Hydroxy*-9-*phenyl*-10-*methyl*-9 : 10-*dihydroanthracene*, m. p. 162° (decomp.), is converted by a similar process into the known 10-phenyl-9-methylanthracene, m. p. 116°.

1-Methylanthraquinone and magnesium phenyl bromide give 9 : 10-*dihydroxy*-9 : 10-*diphenyl*-1-*methyl*-9 : 10-*dihydroanthracene*, m. p. 236°, converted by formic acid and sodium formate at the b. p. into 1-*methyl*-9 : 10-*dihydroanthracene*, m. p. 194°. The similarly obtained pair of 2-methyl compounds have m. p. 238° and 214°, respectively (zinc and acetic acid reduction). Methoxyphenylanthrone (above), is converted by magnesium *o*-tolyl bromide into 10-*hydroxy*-9-*methoxy*-9-*phenyl*-10-o-*tolyl*-9 : 10-*dihydroanthracene*, m. p. 168°, whence the above-mentioned 9-phenyl-10-*o*-tolylanthracene, m. p. 257—258°, results. The corresponding pair of 10-m-*tolyl* compounds have m. p. 209—210° and 182—183°, respectively.

[With W. Stoffers.]—9-*Lithiofluorene* is obtained when lithium ethyl reacts with fluorene, and 9-*sodiofluorene* when sodium triphenylmethyl so reacts. Either compound is converted by carbon dioxide into β-*fluorene*-9-*carboxylic acid*, m. p. 232°. This, like the known (α-) acid, m. p. 222° (decomp.), affords fluorene when heated in aqueous-alkaline solution, a fact which establishes the chemical similarity of the acids, which with diazomethane give the same *methyl* ester, m. p. 63°, b. p. 193°/14 mm., together with some dimethyl bisdiphenylenesuccinate, m. p. 234°. The corresponding acid (see above) affords the ester, m. p. 63°, when kept in methyl-alcoholic sulphuric acid.

9-Lithiofluorene is converted by diphenylmethyl bromide into the known 9-benzhydrylfluorene (9-diphenylmethylfluorene), m. p. 217°, together with a *stereoisomeride*, m. p. 187° (9-sodiofluorene gives only the first isomeride), obtained as the main product (traces of isomeride, m. p. 217°) when sodium diphenylmethyl acts on 9-chlorofluorene. The identity of the lower-melting isomeride is shown by its conversion (potassium; carbon dioxide) into α-fluorene-9-carboxylic acid, together with a little diphenylacetic acid and diphenylmethane. The stereoisomerides appear distinct under cathode rays (absence of dimorphism).

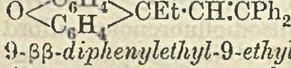
Fluorenone dimethylacetal, m. p. 87—88°, from 9 : 9-dichlorofluorene, gives 9-sodio-9-methoxyfluorene (when treated with sodium), converted by carbon dioxide into 9-*methoxyfluorene*-9-*carboxylic acid*, m. p. 172—173°, and by methyl chloroformate into the corresponding methyl ester, m. p. 124° (also obtainable using diazomethane), which is identical with the ester obtained by Klinger (A., 1912, i, 701), and, when hydrolysed, gives the acid, m. p. 192° (decomp.), described by this author. Lithium may replace sodium in the above. Sodiomethoxyfluorene and methyl iodide give the known methoxymethylfluorene.

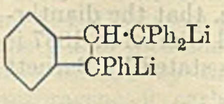
Treatment of lithiofluorene with iodine or with 9-chlorofluorene produces bisdiphenylylene-ethane. 9-Methoxy-9-phenylfluorene, from the corresponding chloro-compound, does not react at all readily with lithium, but with sodium, followed by carbon dioxide, produces 9-phenylfluorene-9-carboxylic acid. 9-Phenylfluorenol, benzyl alcohol, and hydrogen chloride give 9-*benzyloxy*-9-*phenylfluorene*, m. p. 141·5°, which may be used instead of the methoxy-compound.

Diphenylmethylene chloride converts disodiobenzophenone into α-benzpinacolin, yet with disodiofluorenone it gives 10-keto-9 : 9-diphenyl-9 : 10-dihydrophenanthrene, m. p. 193—194°. Similarly, 9 : 9-dichlorofluorene and disodiofluorenone afford 10-keto-9 : 9-diphenylylene-9 : 10-dihydrophenanthrene. On the other hand, disodiobenzophenone and dichlorofluorene give, besides the expected *diphenylylene diphenylethylene oxide*, m. p. 228°, two stereoisomeric 9-diphenylmethylenefluorenes, one, m. p. 225°, also obtained by heating 9-benzhydrylfluorenol with acetyl chloride, identical with that already known, the *isomeride* having m. p. 213°. Both on reduction afford 9-diphenylmethylfluorene, also formed by the action of sodium, followed by alcohol, on the isomeride, m. p. 225°. Mercury converts the sodium compounds of either isomeride into the hydrocarbon of higher m. p. When the above oxide, m. p. 228°, is heated with acetyl chloride it gives the two hydrocarbons, together with 9-benzoyl-9-phenylfluorene (proof of constitution).

Fluorenone is converted by magnesium *iso*propyl chloride into 9-*fluorenyl*iso*propylcarbinol*, m. p. 124°, transformed by way of the chloride (pyridine) into 9-iso*propylidenefluorene*, m. p. 113°, stereoisomeric with Courtot's compound, m. p. 89° (A., 1916, i, 475). 9-Fluorenyldiphenylcarbinol is converted by boiling acetyl chloride into the diphenylmethylenefluorene, m. p. 225°, which, together with its isomeride and the last-named carbinol, are formed when benzophenone acts on 9-lithiofluorene.

III. New type of compound with bivalent carbon. [With B. BENEDIKT and A. WIEGANDT.]—Tetraphenylallene reacts readily with sodium (potassium also reacts) to give the *radical*, $\mathrm{CPh_2Na\cdot\overset{\vdots}{\underset{\vdots}{C}}\cdot CPh_2Na}$, converted by alcohol into ααγγ-tetraphenylpropylene, $\mathrm{CHPh_2\cdot CH{:}CPh_2}$, no doubt by way of the free radical $\mathrm{CHPh_2\cdot\overset{\vdots}{\underset{\vdots}{C}}\cdot CHPh_2}$. Carbon dioxide converts the sodium compound into the *sodium* salt, $\mathrm{CO_2Na\cdot CPh_2\cdot\overset{\vdots}{\underset{\vdots}{C}}\cdot CPh_2\cdot CO_2Na}$, the aqueous solution of which soon deposits the *sodium* salt ($+3H_2O$) of *ααγγ-tetraphenylvinylacetic acid*, $\mathrm{CPh_2{:}CH\cdot CPh_2\cdot CO_2H}$, m. p. 179°. *Ethyl* β-*phenylcinnamate*, b. p. 207°/17 mm., from benzophenone and ethyl bromoacetate (Posner, A., 1911, i, 52), decomposing the intermediate hydroxy-ester by Rupe's method (cf. A., 1914, i, 281, and previous papers), is converted by magnesium phenyl bromide into ααγγ-tetraphenylallyl alcohol, and the latter is converted into the ethyl ether (Ziegler, A., 1924, i, 308). Treatment of the ether with sodium, followed by carbon dioxide, gives the sodium salt ($+3H_2O$) and the acid, m. p. 179°, the constitution of which is thus proved.

The behaviour of various reagents towards the disodium compound (A) from tetraphenylallene and the monosodium compound, $\mathrm{CPh_2Na\cdot CH{:}CPh_2}$ (B), obtained from the last-named ether and sodium has been compared. Methyl iodide converts A or B at the ordinary temperature into *ααγγ-tetraphenyl-γ-methylpropylene* (*ααγγ-tetraphenyl-*Δ^{α}*-butene*), $\mathrm{CPh_2Me\cdot CH{:}CPh_2}$, m. p. 111°, which does not decolorise bromine nor undergo catalytic hydrogenation, whereas 9-ββ-diphenylvinyl-9-ethylxanthen,  $\mathrm{O{<}^{C_6H_4}_{C_6H_4}{>}CEt\cdot CH{:}CPh_2}$, is readily hydrogenated to 9-ββ-*diphenylethyl-9-ethylxanthen*, m. p. 118—119°. At temperatures not above —20°, A is converted by methyl iodide into tetraphenylallene (C), whilst B gives the above propylene. Both A and B react with chloromethyl ether to give *δ-methoxy-ααγγ-tetraphenyl-*Δ^{α}*-butene*, m. p. 124—125°, readily hydrogenated to *methyl ββδδ-tetraphenylbutyl ether*, m. p. 87·5—89°. Methyl chloroformate reacts with A, giving *methyl ααγγ-tetraphenylvinylacetate*, m. p. 117—118°, also obtained by treating the corresponding acid with diazomethane. Ethylthiocarbimide converts A or B into the *thioethylamide*, m. p. 171—173°, of the last acid. αγ-Dibromopropane converts A into C, but B into *ζ-bromo-ααγγ-tetraphenyl-*Δ^{α}*-hexene*, m. p. 120—121°. Iodine converts A into C, and B into a *hydrocarbon*, $C_{27}H_{22}$, m. p. 129—130°, possibly a triphenylhydrindene. Mercury has no action on A, further evidence in support of its assumed structure.



Lithium reacts with tetraphenylallene to give a product (annexed formula) which with alcohol affords 1-*phenyl*-2-*diphenylmethylbenz*cyclo*butene*, m. p. 184°, which exhibits interesting colour reactions with acids, and gives, as the main product of bromination, a *tribromo*-derivative, m. p. 212° (decomp.). The *cyclo*butene does not combine, but reacts, with sodium, the product giving, with carbon dioxide, an *acid*, $\mathrm{C_{27}H_{21}\cdot CO_2H}$, m. p. not below 300°. Lithium ethyl converts the butene into its *lithio*-derivative, $C_{27}H_{21}Li$. The *cyclo*butene is readily hydrogenated to a *hexahydro*-derivative, $C_{27}H_{28}$, the fused benzene ring being the one reduced (reasons given). The original dilithium compound is converted by iodine in benzene or by mercury into a *hydrocarbon*, $C_{27}H_{20}$, m. p. 186°, not reducible catalytically, although converted by sodium and amyl alcohol or by phosphorus and hydriodic and acetic acids into a *hydrocarbon*, $C_{27}H_{22}$, m. p. 167—168°. The hydrocarbon, m. p. 186°, when treated first with sodium and then with alcohol, gives a *hydrocarbon*, $C_{27}H_{22}$, m. p. 103°.

2 : 3-Diphenylindone (preparation improved) with magnesium phenyl bromide affords 1-hydroxy-1 : 2 : 3-triphenylindene (Kohler, A., 1908, i, 777), reduced by phosphorus and hydriodic and acetic acids to 1 : 2 : 3-*triphenylhydrindene*, m. p. 153°. 1 : 2 : 3-Triphenylindene (Kohler) is obtainable by treating its 1-methoxy-derivative with sodium and the product with alcohol. *Diphenylbenzylacetyl chloride*, m. p. 90—91°, in presence of aluminium chloride and carbon disulphide, passes into a product which, after treatment with magnesium phenyl bromide, gives 1-*hydroxy*-1 : 2 : 2-*triphenylhydrindene*, m. p. 172—173°. The latter, when reduced (phosphorus method), affords 1 : 2 : 2-*triphenylhydrindene*, m. p. 142°, also obtained by the action at 140° of acetic anhydride and a little sulphuric acid on 1 : 2 : 2 : 3-*tetraphenylpropyl alcohol*, m. p. 141—142°, the latter being obtained by treating the product of the action of sodium on the methyl ether of diphenyldibenzylcarbinol with benzaldehyde:

$$\mathrm{CH_2Ph\cdot CPh_2\cdot OMe} \longrightarrow \mathrm{CH_2Ph\cdot CPh_2Na} \longrightarrow$$
$$\mathrm{CH_2Ph\cdot CPh_2\cdot CHPh\cdot OH} \longrightarrow \text{triphenylhydrindene.}$$

When ααβγ-tetraphenylpropane-αβ-diol is treated with acetyl chloride it gives benzyl triphenylmethyl ketone (obtained by Orékhov, A., 1919, i, 272, by treating the diol with sulphuric acid) together with 1 : 2 : 2 : 3-tetraphenylpropyl alcohol (obtained by a third process, see above, by treating with benzoyl chloride the product of the action of sodium on the methyl ether of diphenylbenzylcarbinol) and a *substance*, m. p. 126—127°, which may be 2-hydroxy-1 : 1 : 2-triphenylhydrindene.

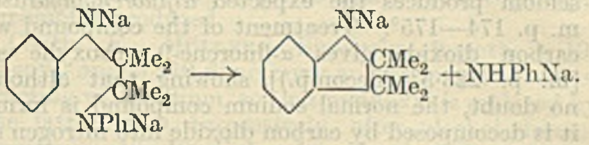
Diphenyl-*o*-tolylmethyl chloride, best obtained from the corresponding carbinol by passing hydrogen chloride into a benzene solution of the latter containing acetyl chloride, is converted by sodium amalgam into a sodio-compound, which with carbon dioxide affords *diphenyl*-o-*tolylacetic acid*, m. p. 240° (*ethyl* ester, from the sodio-compound and ethyl chloroformate, has m. p. 100—101°). The corresponding acid *chloride*, m. p. 86·5—87°, does not undergo ring-closure ($\cdot COCl + CH_3\cdot \longrightarrow \cdot CO\cdot CH_2\cdot$) when treated with boiling pyridine, but merely passes into the acid *anhydride*, m. p. 197°.

Methyl s-*diphenylethane*-2-*carboxylate*, b. p. 195—196°/25 mm., reacts with magnesium phenyl bromide to produce o-β-*phenylethylphenyldiphenylcarbinol*, $CH_2Ph\cdot CH_2\cdot C_6H_4\cdot CPh_2\cdot OH$, m. p. 103°, convertible into the corresponding *chloride*, m. p. 128—130°. When the latter is heated with quinoline at 150° it affords 1 : 1 : 2-*triphenylhydrindene*, m. p. 83°.

The following hydrocarbons were prepared during the investigation of the above *benz*cyclo*butene*. 9-*Diphenylmethyl*-9 : 10-*dihydroanthracene*, m. p. 207·5°, is formed by sodium–amyl alcohol reduction of 9-diphenylmethylanthrone. 9-ββ-*Diphenylethylfluorene*, m. p. 107°, is obtained by similar reduction of 9-ββ-*diphenylvinylfluorene*, m. p. 111—112°, which is formed by the action of boiling pyridine on the 9-β-chloro-compound corresponding with 9-β-*hydroxy*-ββ-*diphenylethylfluorene*, $C_{12}H_8{:}CH\cdot CH_2\cdot CPh_2\cdot OH$, m. p. 121°, the latter being prepared from magnesium phenyl bromide and ethyl fluorenylacetate. 9 : 10-*Diphenyl*-9-*methyl*-9 : 10-*dihydroanthracene*, m. p. 171°, is formed by reducing (phosphorus and hydriodic and acetic acids) 10-hydroxy-9 : 10-diphenyl-9-methyl-9 : 10-dihydroanthracene, m. p. 183—184°, this substance being prepared by treatment with methyl iodide of the sodio-compound formed by the action of sodium on 9-hydroxy-10-methoxy-9 : 10-diphenyldihydroanthracene. 9-Methoxy-9-phenylanthrone is reduced (sodium and amyl alcohol) to 9-phenyl-9 : 10-dihydroanthracene (m. p. 87°, above). The *hydrazone*, m. p. 142°, of the last-named anthrone is converted by sodium ethoxide into 9-phenylanthracene. 9-*Phenyl*-10-*benzyl*-9 : 10-*dihydroanthracene*, m. p. 119°, is formed by treating, first with sodium and then with alcohol, 9-phenyl-10-benzylanthracene (m. p. 151°; lit. 155°). The latter is obtained by phosphorus and hydriodic acid–acetic acid reduction of 10-*hydroxy*-9-*methoxy*-9-*phenyl*-10-*benzyl*-9 : 10-*dihydroanthracene*, m. p. 151°, formed when magnesium benzyl chloride reacts with methoxyphenylanthrone.

IV. Addition of sodium to carbon–nitrogen and to nitrogen–nitrogen double linkings. Acetophenone anil and sodium afford the *compound* CPhMeNa·NPhNa, converted by alcohol into phenyl-α-phenylethylamine, and by carbon dioxide into the *sodium* salt, $CO_2Na\cdot CPhMe\cdot NPh\cdot CO_2Na$. Fluorenone anil (9-anilofluorene) similarly gives rise to 9-anilinofluorene and 9-*anilinofluorene*-9-*carboxylic acid*, m. p. 217°. Benzylidene-ethylamine gives benzylethylamine, and acetophenone-benzylimide gives α-phenylethylbenzylamine. Fluorenoneimine (9-iminofluorene) gives a sodium compound decomposed by alcohol into iminofluorene and occasionally a little 9 : 9-difluorenylamine, and giving by the carbon dioxide process not the expected acid, which is very unstable, but 9-aminofluorene. Acetone anil affords (sodium, followed by alcohol) 2 : 2 : 3 : 3-tetramethylindoline (?), m. p. 39°, b. p. 148—149°/21 mm. (cf. Knoevenagel, A., 1922, i, 1060), and aniline, so that the original action of sodium is probably :

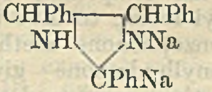
$2NPh{:}CMe_2 + 2Na \longrightarrow$



Similarly treated, the anil of methyl ethyl ketone gives aniline, methane, and 3-*methyl*-2 : 3-*diethyl*iso-*indole*, b. p. 152—153°/12 mm. (*methiodide*, m. p. 242°).

[With R. Israel.]—Hydrobenzamide and sodium give the *compound* of formula (A), converted by alcohol into 2 : 4 : 5-*triphenyltetrahydroglyoxaline*, m. p. 270—271° (*hydrochloride*), also obtained from the

(A)



(B)

disodium compound (B) formed by amarine, or by the catalytic hydrogenation of the latter. Acridine and sodium give two compounds, the formulae of which follow from the fact that 5 : 10-dihydroacridine and *tetrahydro*-5 : 5′-*diacridyl*, m. p. 279°, result by treatment with alcohol. The diacridyl is apparently identical with that known to be formed when acridine is reduced with sodium amalgam and alcohol, which has hitherto been regarded as the 10 : 10′-compound. When the acridine–sodium compound is treated with benzoyl chloride, there is formed, as the least soluble product, NN′-*dibenzoyltetrahydro*-5 : 5′-*diacridyl*, m. p. 305°. Again, sodium–carbon dioxide treatment of acridine gives 5 : 10-*dihydroacridine*-5-*carboxylic acid*, m. p. 229° (decomp.), and evidently also the *NN′*-dicarboxylic acid of the diacridyl, for this substance is deposited shortly after the reaction product is dissolved in water.

5-Phenylacridine adds 2 atoms of sodium in the 5- and 10-positions, so that alcohol converts the product into 5 : 10-dihydroacridine, and carbon dioxide affords 5-*phenyl*-5 : 10-*dihydroacridine*-5-*carboxylic acid*, m. p. 225—227° (decomp.). Lophine (2 : 4 : 5-triphenylglyoxaline) reacts with sodium to give the 1-*sodio*-derivative and hydrogen. Treatment with carbon dioxide therefore regenerates lophine.

Phenazine reacts with sodium, but the product is unworkable. When the sodium ketyl prepared from phenyl diphenylyl ketone is added to phenazine in ether there is formed the additive *compound* of phenazine (1 mol.) with 5 : 10-disodio-5 : 10-dihydrophenazine (1 mol.). This, and the analogous *dipotassio*-additive compound, are converted by water into the known phenazine–dihydrophenazine additive compound (the so-called “ quinhydrone ”).

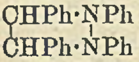
Acetophenone ketazine, CPhMe:N·N:CPhMe, combines with sodium to give the *compound* CPhMeNa·NNa·NNa·CPhMeNa. The similar *compound* from benzophenone ketazine, when decomposed with alcohol in an inert atmosphere, gives *s*-dibenzhydrylhydrazine, m. p. 138° (sinters 131°). Darapsky, who obtained only the impure hydrazine, gives m. p. 120—123° (A., 1903, i, 367). The normally derived *sodium* salt of the tetracarboxylic acid is described. Fluorenone ketazine and sodium give a compound the (alcohol) decomposition of which only seldom produces the expected *difluorenylhydrazine*, m. p. 174—175°. Treatment of the compound with carbon dioxide gives α-fluorene-9-carboxylic acid [m. p. 223·5° (decomp.)], showing that although, no doubt, the normal sodium compound is formed, it is decomposed by carbon dioxide into nitrogen and the above acid.

[With A. Michael.]—Benzylideneazine forms the *disodium* compound, $\mathrm{(CHPh{:}N{\cdot}NNa{\cdot}CHPh{\cdot})_2}$, converted by carbon dioxide into the *sodium* salt of the expected dicarboxylic acid and by alcohol into the expected *NN′-dibenzylidene-αβ-diphenylethane-αβ-dihydrazine*, m. p. 117—118°.

Benzophenone hydrazone is converted by sodium into the *compound*, $\mathrm{CPh_2{:}N{\cdot}NHNa}$, reacting with methyl iodide to give the *methiodide*, m. p. 226·5°, of benzophenone methylhydrazone. Benzophenone diphenylhydrazone gives sodium diphenylamine and the *compound* $\mathrm{CPh_2Na{\cdot}NNa_2}$, decomposed (alcohol) into benzhydrylamine. Benzophenone phenylhydrazone behaves similarly. The *anil* formed from benzophenone and benzhydrylamine has m. p. 153°. Decomposition of the original sodium compound–ether mixture with carbon dioxide gave aniline, the anil and *benzhydrylammonium carbonate*, which when heated in ethyl acetate (or alone at 56°) is converted into a substance, $\mathrm{(C_{15}H_{17}O_2N)}_x$, m. p. 145°, evidently identical with the supposed tribenzhydrylamine obtained by decomposition of benzhydrylammonium carbamate. Benzophenone phenylmethylhydrazone behaves similarly to the phenylhydrazone.

Azomethane gives the *compound*, $\mathrm{NMeNa{\cdot}NMeNa}$, convertible into hydrazomethane or into the *sodium* salt of hydrazomethane-NN′-dicarboxylic acid. Tetraphenyltetrazine and sodium give nitrogen and sodiodiphenylamine (2 mols.).

[With R. Israel and H. Willstädt.]—The above product from sodium and benzophenone anil reacts with mercury, methyl iodide, benzoyl chloride, ethyl benzoate, or phenylthiocarbimide, giving the original anil. The product from sodium and benzylideneaniline is unaffected by mercury, is converted by phenylthiocarbimide into (the *disodium* derivative of) *αβ-bis-s-diphenylthiocarbamido-αβ-diphenylethane*, $\mathrm{(NHPh{\cdot}CS{\cdot}NPh{\cdot}CHPh{\cdot})_2}$, m. p. 263°, by methyl iodide into *αβ-bismethylanilino-αβ-diphenylethane*, $\mathrm{(NPhMe{\cdot}CHPh{\cdot})_2}$, m. p. 127°, by diphenylmethylene chloride into tetraphenylethylene, and by ethyl benzoate or benzaldehyde into the *compound*,

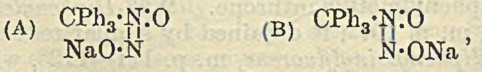


$$\begin{array}{l}\mathrm{CHPh{\cdot}NPh}\\ \mathrm{CHPh{\cdot}NPh}\end{array}$$

, m. p. 153—154°.

V. Experiments with triphenylmethyl and sodium triphenylmethyl. [With C. Bresiewicz and H. Ender.]—Sodium triphenylmethyl reacts with nitrous oxide in ethereal solution to give the red *sodium triphenylmethyl diazotate*, $\mathrm{CPh_3{\cdot}N{:}N{\cdot}ONa}$. Continued action of nitrous oxide produces a yellow substance, which is being investigated. The diazotate is violently decomposed by alcohol, triphenylcarbinol being formed. Water produces a tar.

When nitric oxide is passed into an ethereal solution of sodium triphenylmethyl, a bluish-red *compound* separates (not more than 1 mol. of oxide must be used) which may be either $\mathrm{CPh_3{\cdot}\underset{\vdots}{N}{\cdot}ONa}$ or $\mathrm{CPh_3{\cdot}N\underset{\vdots}{Na}{:}O}$. If more nitric oxide is passed into the suspension, the bluish-red compound is replaced by a bright yellow sodium salt, A. If sodium amalgam is present, the bluish-red compound is still produced, but passes later into a second bright yellow sodium salt, B, the solution then being bluish-green. Either A or B, when treated in ethereal suspension with sodium amalgam, affords sodium triphenylmethyl and sodium hyponitrite. Acidification of an aqueous solution of A produces triphenylcarbinol and nitrous oxide, whilst B under similar conditions affords the corresponding acid, which undergoes conversion into carbinol etc. only on long keeping or on warming. A and B are regarded as being the sodium salts of *syn*- and *anti*-forms of iso*nitrosotriphenylmethylhydroxylamine*, respectively :



$$\text{(A)}\quad \begin{array}{l}\mathrm{CPh_3{\cdot}N{:}O}\\ \mathrm{NaO{\cdot}N}\end{array}\qquad \text{(B)}\quad \begin{array}{l}\mathrm{CPh_3{\cdot}N{:}O}\\ \mathrm{\phantom{CPh_3{\cdot}}N{\cdot}ONa}\end{array},$$

whilst the true triphenylmethylnitrosohydroxylamine is probably present in the bluish-green solution mentioned above. A crystallises $+\mathrm{EtOH}$ or $+\mathrm{C_6H_6}$ and may be converted into the *silver*, *mercuric*, *cupric*, *ferric*, and *lead* salts. B crystallises $+\mathrm{EtOH}$, and gives rise to salts (identical with the above ?) of other metals.

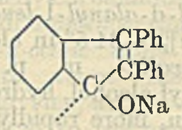
[With C. Bresiewicz and E. Rubens.]—When an ethereal solution of triphenylacetyl chloride is added to one of sodium triphenylmethyl, *hexaphenylacetone* (*bistriphenylmethyl ketone*), $\mathrm{CPh_3{\cdot}CO{\cdot}CPh_3}$, m. p. 80—81° results. In presence of excess of the sodium compound it passes into a brownish-red, crystalline *ketyl*, $\mathrm{CPh_3{\cdot}C(CPh_3){<}_{ONa}}$, which may be decomposed into hexaphenylacetone and *hexaphenyl*iso*propyl alcohol* (not described).

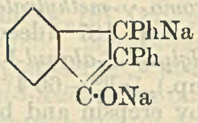
[With W. Stoffers.]—Sodium triphenylmethyl undergoes the following reactions : (1) Ethylthiocarbimide gives the *ethylamide*, m. p. 143°, of triphenylthioacetic acid. (2) Phenylthiocarbimide gives *triphenylthioacetanilide*, m. p. 157°. (3) Allylthiocarbimide gives the *allylamide*, m. p. 131—132°, of trithioacetic acid. (4) Phenylcarbimide gives triphenylacetanilide. (5) Ethyl chloroformate gives ethyl triphenylacetate. (6) Acetyl, *iso*propyl, or *tert.*-butyl chloride gives triphenylmethane. (7) Chloromethyl ether gives *βββ-triphenylethyl methyl ether*, m. p. 137°.

Sodium diphenylmethyl, readily obtained by treating benzhydryl methyl ether with powdered sodium in ether (cf. Ziegler and Thielmann, A., 1923, i, 921), gives the following reactions : (1) Phenylthiocarbimide gives diphenylthioacetanilide. (2) Benzophenone gives *ααββ-tetraphenylethyl alcohol*, m. p. 236°. (3) Fluorenone gives 9-*hydroxy*-9-*diphenylmethylfluorene*, m. p. 183°.

[With T. Kohler.]—Pure sodium diphenylmethyl is obtained if mercury dibenzyl is converted in benzene into sodium benzyl, and this is digested with diphenylmethane.

VI. Diarylketone-alkali metal additive compounds. [With E. Müller.]—2 : 3-Diphenylindone is converted by sodium in ether first into the *ketyl* and then into the *disodium* compound,





Alcohol converts the second compound into 2 : 3-diphenyl-1-hydrindone, methyl iodide affords 2 : 3-*diphenyl*-2 : 3-*dimethyl*-1-*hydrindone*, m. p. 166—167°, and carbon dioxide gives 2 : 3-*diphenyl*-1-*hydrindone*-3-*carboxylic acid*, m. p. 181° (decomp.).

[With H. Willstädt.]—Phenyl diphenylyl ketone sodium mono- and di-ketyls react with phenylthiocarbimide to give the compound, $\mathrm{NPhNa{\cdot}CS{\cdot}CS{\cdot}NPhNa}$ (cf. I*e*, above).

[With A. Knorr.]—Benzyl chloride reacts with the disodium derivative of benzophenone according to the scheme : $\mathrm{CAr_2Na{\cdot}ONa(+R{\cdot}X)} \longrightarrow \mathrm{CAr_2R{\cdot}ONa}$, and with that of phenyl diphenylyl ketone thus : $\mathrm{CAr_2Na{\cdot}ONa(+2R{\cdot}X)} \longrightarrow \mathrm{CAr_2R{\cdot}OR}$. Diphenylbenzylcarbinol is the product of the first and the *benzyl ether*, m. p. 164—165°, of *phenyl*-4-*diphenylylbenzylcarbinol* that of the second reaction. This carbinol, formed by the interaction of magnesium benzyl chloride and phenyl diphenylyl ketone, has m. p. 129—130° and is converted by benzyl alcohol, benzene, and hydrogen chloride not into the above ether, but into αβ-*diphenyl*-α-4-*diphenylylethylene*, m. p. 134—135°. Methyl iodide reacts less simply with the disodium derivative of phenyl diphenylyl ketone, the products being : (1) *phenyldiphenylylmethylcarbinol*, (2) the corresponding methyl ether, (3) p-*tolyl* 4-*diphenylyl ketone*, m. p. 133—134°, converted by sodium, followed by alcohol, into 4-*phenyl*-4′-*methylbenzhydrol*, m. p. 110°, and also obtainable from diphenyl and *p*-toluoyl chloride in presence of aluminium chloride. The carbinol and ether (1 and 2) are not isolable, but their presence is shown by the conversion of the mixture into as-*phenyldiphenylylethylene*, m. p. 94°. The carbinol (1), m. p. 105—106°, is obtainable from phenyl diphenylyl ketone and magnesium methyl iodide, and readily affords the *methyl ether*, m. p. 117°. 2-*Phenylbenzophenone* (*phenyl* 2-*diphenylyl ketone*), synthesised for comparison purposes, has m. p. 90°, and results when magnesium phenyl bromide reacts with 2-*cyanodiphenyl*, m. p. 41°, b. p. 175°/13 mm. The latter is formed from phosphorus pentachloride and *diphenyl*-1-*carboxylamide*, m. p. 176°, obtained from the corresponding *chloride*, b. p. 169°/16 mm.

VII. Some scissions using alkali metals. [With H. Willstädt.]—When powdered sodium is used for the scission of benzophenone dimethylacetal in place of the potassium–sodium alloy used by Ziegler and Thielmann (*loc. cit.*) (these authors decomposed the product with carbon dioxide and obtained benzilic acid methyl ether), there is formed, after decomposition by alcohol, diphenylmethylcarbinol. Decomposition with carbon dioxide produces some benzilic acid and some of its methyl ether, whilst mercury produces diphenylmethylcarbinol. The scission reaction must therefore be : $\mathrm{CPh_2(OMe)_2} \longrightarrow \mathrm{CPh_2{\cdot}CNa{\cdot}OMe} \longrightarrow \mathrm{CPh_2{\cdot}CMe{\cdot}ONa}$, the intermediate compound accounting for the benzilic acid, etc.

Although it was expected that sodium would convert benzpinacolin diphenyl ether into benzpinacol diphenyl ether, the latter is not isolated, but passes into the compound $\mathrm{CPh_2{\cdot}CNa{\cdot}OPh}$, so that triphenylcarbinol is produced.

[With E. Müller.]—Similarly, 9-methoxy-10-phenyl- and 9 : 10-dimethoxy-anthracene, instead of reacting with sodium, so that methoxyl is replaced by the latter, give, respectively, after alcohol decomposition, 10 : 10′-*diphenyl*-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthranyl*, m. p. 260° (also obtained by the sodium–alcohol process from 10 : 10′-diphenyl-9 : 9′-dianthranyl), and 9-hydroxy-10-methoxyanthracene (isolated as the benzoate). Iodine converts the second sodium product into dimethoxydianthrone.

E. E. Turner.

Quantitative analysis of organo-lead compounds. H. Gilman and J. Robinson (J. Amer. Chem. Soc., 1928, **50**, 1714—1716).—Derivatives in which lead is directly attached to aryl groups cannot be satisfactorily analysed by existing methods (cf. Grüttner and Krause, A., 1916, i, 684 ; Calingaert, A., 1925, i, 798). Correct results are obtained by oxidising the sample (0·5 g.) by means of sulphuric and nitric acids (cf. Noyes and Bray, A., 1907, ii, 391), completely removing the nitric acid, and separating the lead sulphate in the usual way.

H. E. F. Notton.

Hydrolysis of polypeptides by *N*-alkali and by the enzymes of the pancreas. E. Abderhalden and H. Brockmann (Fermentforsch., 1928, **9**, 430—438).—The *chloroacetyl*, m. p. 136—137° ; *glycyl*, m. p. 241—242° ; dl-α-*bromopropionyl*, m. p. 157—158° ; dl-*alanyl*, m. p. 254—255° (decomp.) ; *benzoyl*, m. p. 189—190° ; d-α-*bromo*-γ-*methylvaleryl*, m. p. 150—152° (decomp.), $[\alpha]_D^{20}$ −33·2° in alcohol, and l-*leucyl*, m. p. 240° (decomp.), derivatives of *dl*-α-aminobutyryl-*dl*-α-aminobutyric acid are prepared by the usual methods, also *chloroacetyl*-dl-*leucyl*-dl-α-*aminoheptoic acid*, m. p. 147·5°, and *glycyl*-dl-*leucyl*-dl-α-*aminoheptoic acid*, m. p. 240° (decomp.). The dipeptide and the *l*-leucyl tripeptide are not hydrolysed by *N*-sodium hydroxide in 123 hrs. at 37° (cf. this vol., 81) ; in the cases of the glycyl and alanyl derivatives, glycine and alanine are eliminated. The benzoyl derivative is hydrolysed slowly, without formation of free benzoic acid. Of glycyl- and *dl*-leucyl-*dl*-aminoheptoic acids, the former is hydrolysed but not the latter. Glycine is slowly eliminated from glycyl-*dl*-leucyl-*dl*-α-aminoheptoic acid. Since *dl*-α-aminobutyryl-*dl*-α-aminobutyric acid is decomposed in part by pancreas enzymes, it would appear to be a mixture of the *dd*- and *ll*-modifications, not of *dl*- and *ld*-forms. Pancreas enzymes do not hydrolyse the benzoyl derivative, but the glycyl- and alanyl-tripeptides are attacked, the former more slowly, the latter more rapidly than by alkali.

F. E. Day.

Enzymic decomposition of polypeptides containing *l*-hydroxyproline. E. Abderhalden and W. Köppel (Fermentforsch., 1928, **9**, 439—445).—The following substances have been prepared.

Chloroacetyl-l-*hydroxyproline*, m. p. 160°; *glycyl*-l-*hydroxyproline*, m. p. 215°, $[\alpha]_D^{20}$ −50·79° in water; dl-α-*bromo*-γ-*methylvaleryl*-l-*hydroxyproline*, m. p. 155°; dl-*leucyl*-l-*hydroxyproline*, m. p. 234°, $[\alpha]_D^{20}$ −36·97° in water. Glycyl-*l*-hydroxyproline is hydrolysed by erepsin, but not by pepsin or trypsin. None of these enzymes attacks *dl*-leucyl-*l*-hydroxyproline. *N*-Hydrochloric acid is practically without action on either dipeptide at 37°, at which temperature *N*-sodium hydroxide hydrolyses glycyl-*l*-hydroxyproline, but not the leucyl compound. During the preparation of *dl*-leucyl-*l*-hydroxyproline, a substance, m. p. 168°, was isolated, apparently *hydroxy*-γ-*methylvaleryl*-l-*hydroxyproline*. F. E. DAY.

Enzymic decomposition of polypeptides. E. ABDERHALDEN and H. BROCKMANN (Fermentforsch., 1928, 9, 446—461).—Improvements in the methods for preparing *d*-alanine, *d*-α-bromo-γ-methylvaleryl chloride, and *l*-α-bromopropionyl chloride are described, and from these the synthesis of *glycyl*-d-*alanyl*-l-*leucylglycyl*-d-*alanine* has been carried out. Chloroacetyl-*d*-alanine and its ammonium salt, from which glycyl-*d*-alanine is obtained by heating with alcoholic ammonia; *d*-α-bromo-γ-methylvalerylglycyl-*d*-alanine, m. p. 132—133°, $[\alpha]_D^{20}$ +31·2°±0·3° in alcohol; these constants are higher than those given by Fischer (A., 1909, i, 366) and *d*-α-bromo-γ-methylvaleramide was isolated as a by-product. Next *l*-leucylglycyl-*d*-alanine and its d-α-*bromo*iso*propionyl* derivative, m. p. 157—158°, $[\alpha]_D^{20}$ +12·9° in alcohol, −27·95° in water, d-*alanyl*-l-*leucylglycyl*-d-*alanine* (decomp. 240°), $[\alpha]_D^{20}$ −28·0° in water, *chloroacetyl*-d-*alanyl*-l-*leucylglycyl*-d-*alanine*, m. p. 143—147°, $[\alpha]_D^{20}$ −45·5° in alcohol, and finally glycyl-*d*-alanyl-*l*-leucylglycyl-*d*-alanine, decomp. 232°, $[\alpha]_D^{20}$ −70·6° in water. The pentapeptide is precipitated by saturated ammonium sulphate and gives a strong red biuret reaction. At 37° it is rapidly hydrolysed by trypsin (p_H 8·4) and by *N*-sodium hydroxide, less rapidly by erepsin (p_H 7·8), and only slightly by *N*-hydrochloric acid.

Trypsin is without action on *l*-leucylglycyl-*d*-alanine, which is rapidly hydrolysed by erepsin, mainly at the leucyl–glycyl linking; *d*-alanyl-*l*-leucylglycyl-*d*-alanine is hydrolysed by both enzymes at a moderate rate. The results may be to some extent vitiated by imperfect separation of the enzymes, but are confirmatory of the hydrolysis of pentapeptides by trypsin (cf. Waldschmidt-Leitz, Grassmann, and Schlatter, A., 1927, 1112). F. E. DAY.

Enzymic decomposition of polypeptides of various composition. E. ABDERHALDEN and H. SICKEL (Fermentforsch., 1928, 9, 462—484).—The preparation of the following substances and the action of erepsin and trypsin on the polypeptides are described: *d*-α-bromo-γ-methylvaleryl-*d*-valine; *l*-leucyl-*d*-valine, hydrolysed by erepsin but not by trypsin; *d*-α-*bromopropionyl*-l-*leucyl*-d-*valine*, m. p. 165°, $[\alpha]_D^{20}$ −34° in alcohol; *d*-*alanyl*-l-*leucyl*-d-*valine*, m. p. 243—245° (decomp.), $[\alpha]_D^{19}$ −60° in water, readily hydrolysed by erepsin, but not by trypsin; a second modification of this substance having similar physical properties, except that its solubility in water at 18° is 4·1 g. per 100 c.c., against 0·44 g. of the chief product, and probably a stable mixture of optical isomerides, unacted on by erepsin; *chloroacetyl*-l-*alanyl*-l-*leucyl*-d-*valine*, m. p. 204—205°, $[\alpha]_D^{20}$ −69·6° in alcohol; *glycyl*-d-*alanyl*-l-*leucyl*-d-*valine*, m. p. 240° (decomp.), $[\alpha]_D^{21}$ −98° in water (+$2H_2O$), hydrolysed by erepsin, little if at all by trypsin; d-α-*bromo*-γ-*methylvalerylglycyl*-d-*alanyl*-l-*leucyl*-d-*valine*, m. p. 187° (decomp.), $[\alpha]_D^{19}$ −34·5° in alcohol; l-*leucylglycyl*-d-*alanyl*-l-*leucyl*-d-*valine*, m. p. 205° (decomp.), $[\alpha]_D^{16}$ −60·4° in methyl alcohol, hydrolysed both by erepsin and by trypsin, more rapidly by a mixture of both enzymes. An attempt to deduce the point of enzymic attack by observation of change of α_D was unsuccessful. F. E. DAY.

Action of erepsin and trypsin on polypeptides containing *d*-glutamic acid. E. ABDERHALDEN and E. ROSSNER (Fermentforsch, 1928, 9, 494—500).—In preparing glycyl-*d*-glutamic acid, the intermediate chloroacetyl-*d*-glutamic acid is best purified as the ammonium salt. d-α-*Bromo*-γ-*methylvalerylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ +24·6° in methyl alcohol, is converted into l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ 25·4° in water, by treatment with 25% aqueous ammonia, since alcoholic ammonia leads to anhydride formation. This compound gives a positive ninhydrin reaction, a bluish-violet biuret reaction, and is not precipitated by saturated ammonium sulphate. It is widely disintegrated by *N*-sodium hydroxide and by 5*N*-hydrochloric acid at 37°; one CO–NH linking is broken by erepsin, but trypsin has practically no action. *l*-Leucyl- and *dl*-leucyl-*d*-glutamic acids are only very slowly and slightly attacked by *N*-alkali, erepsin, or trypsin. Glycyl-*d*-glutamic acid is hydrolysed by *N*-alkali, 5*N*-hydrochloric acid, and erepsin, but not by trypsin. The action of extract of dried pancreas on *l*-leucyl- and glycyl-*d*-glutamic acids is similar to that of erepsin. F. E. DAY.

Enzymic decomposition of polypeptides by erepsin and by trypsin-kinase. Polypeptides containing *l*-cystine. E. ABDERHALDEN and W. KÖPPEL (Fermentforsch., 1928, 9, 516—523).—By the usual methods the authors prepared di-(*d*-alanyl)-*l*-cystine, *di*-(d-α-*bromo*iso*valeryl*-d-*alanyl*)-l-*cystine*, m. p. 155°, $[\alpha]_D^{18}$ −18·6° in alcohol; *di*-(d-*valyl*-d-*alanyl*)-l-*cystine*, $[\alpha]_D^{19}$ −102·6° in *N*-hydrochloric acid; *di*-(d-α-*bromopropionyl*-d-*valyl*-d-*alanyl*)-l-*cystine*, m. p. 163°, $[\alpha]_D^{20}$ +13·4° in alcohol; *di*-(d-*alanyl*-d-*valyl*-d-*alanyl*)-l-*cystine*, $[\alpha]_D^{20}$ − 79·4° in *N*-hydrochloric acid, precipitated by ammonium sulphate; *di*-(d-α-*bromo*-γ-*methylvaleryl*-d-*alanyl*-d-*valyl*-d-*alanyl*)-l-*cystine*, m. p. 164°, $[\alpha]_D^{19}$ +34·3° in alcohol; di-(*l*-leucyl-*d*-alanyl-*d*-valyl-*d*-alanyl)-*l*-cystine, $[\alpha]_D^{18}$ −74·6 in *N*-hydrochloric acid. Erepsin acted rapidly on the tri- and penta-peptides, less strongly on the heptapeptide, not at all on the nonapeptide. The last was attacked readily by trypsin-kinase, the heptapeptide still more vigorously. The tripeptide was not affected, and the pentapeptide only comparatively slowly by trypsin-kinase. The action of these enzymes on di-(*l*-leucyl)-*l*-cystine, di-(*l*-leucylglycyl)-*l*-cystine, and di-(*l*-leucyl-*d*-alanine)*l*-cystine was similar to that on the above tri- and penta-peptides.

F. E. DAY.

Specific adaptation of polypeptidases. E. Abderhalden and E. Schwab (Fermentforsch., 1928, **9**, 501—515).—In continuation of previous attempts to determine the molecular groupings attacked by different enzymes (cf. A., 1927, 1112), the phenylcarbamido-compounds of *dl*-leucylglycine, *glycyl*-dl-*α-aminoheptoic acid*, m. p. 181°, *glycyl*-dl-*α-amino*-n-*octoic acid*, m. p. 185°, *glycyl*-l-*tyrosine*, decomp. about 128°, glycyl-*dl*-serine, *dl*-leucylglycylglycine, and l-*leucylglycyl*-l-*leucine*, an oil, were submitted to the action of erepsin and of trypsin-kinase. All were hydrolysed by the latter, not by the former. Naphthalene-2-sulphonyl derivatives of glycyl-*dl*-leucine, *dl*-leucylglycine, glycyl-*l*-tyrosine, and *glycyl*-dl-*phenylalanine* were hydrolysed by trypsin-kinase, but not naphthalene-2-sulphonylglycylglycine. The latter, also the β-naphthalenesulphonyl derivativesof glycyl-*dl*-leucine and *dl*-leucylglycine, were not hydrolysed by erepsin. Neither enzyme acted on carbethoxyglycylglycine ester. By condensing 2-pyrrolidone-5-carboxyl chloride with *l*-tyrosine ester in chloroform, 2-pyrrolidone-5-carboxyltyrosine, decomp. 250°, and glutamyltyrosine, a syrup, were prepared. The latter was hydrolysed by erepsin and by trypsin. Of dl-*leucyltriglycyl*-dl-*serine* (decomp. above 175°; not precipitated by ammonium sulphate) and *dl*-leucyltriglycyltyrosine, the former was hydrolysed by erepsin, not by trypsin; the latter by trypsin, not by erepsin. Only polypeptides containing certain amino-acids are capable of hydrolysis by erepsin and then only if the amino-group is free (cf. Euler and Josephson, A., 1927, 696). The amino-group thus appears to be the point of attack by erepsin, but not by trypsin. The results suggest the composite nature of both enzymes.

F. E. Day.

Enzymic decomposition of polypeptides of various composition and their behaviour to *N*-alkali. Polypeptides containing mainly *l*-leucine. E. Abderhalden and R. Fleischmann (Fermentforsch., 1928, **9**, 524—533).—*dl*-Leucine was prepared from *iso*valeraldehyde and resolved by fractionation of the brucine salt of its formyl derivative. From it, *l*-leucyl-*l*-leucine; *benzoyl*-l-*leucyl*-l-*leucine*, m. p. 133°, $[\alpha]_D^{20}$ −49·14° in *N*-sodium hydroxide; *phenylcarbamido*-l-*leucyl*-l-*leucine*, m. p. 198°, $[\alpha]_D^{20}$ −68·66° in *N*-sodium hydroxide; *chloroacetyl*-l-*leucyl*-l-*leucine*, m. p. 180—182°, $[\alpha]_D^{20}$ −51·72° in alcohol; *glycyl*-l-*leucyl*-l-*leucine*, m. p. 232—234° (decomp.), $[\alpha]_D^{20}$ −67·01° in alcohol; d-*α-bromo-γ-methylvaleryl*-l-*leucyl*-l-*leucine*, m. p. 212°, $[\alpha]_D^{20}$ −38·04° in alcohol; l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −51·36° in *N*-sodium hydroxide; *chloroacetyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, m. p. 193° (decomp.), $[\alpha]_D^{20}$ −76·19° in alcohol; *glycyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −78·63° in *N*-sodium hydroxide; d-*α-bromo-γ-methylvaleryl*-l-*leucyl*-l-*leucyl*-l-*leucine*, m. p. 224°, $[\alpha]_D^{20}$ −70·55° in alcohol; l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −89·95° in *N*-sodium hydroxide; *chloroacetyl*-l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −83·9° in alcohol; *glycyl*-l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −118° in *N*-sodium hydroxide, d-*α-bromo-γ-methylvaleryl*-l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −94·5° in alcohol, and l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine* were prepared. The last pentapeptide was insoluble even in *N*-alkali. *l*-Leucyl-*l*-leucine and glycyl-*l*-leucyl-*l*-leucine were readily hydrolysed by erepsin, but only slightly by trypsin. None of the polypeptides containing only *l*-leucine was hydrolysed by *N*-sodium hydroxide at 37°, but the glycine was eliminated from the tri-, tetra-, and penta-peptides containing this as the end member of the chain. It is remarkable that in the case of phenylcarbamido-*l*-leucyl-*l*-leucine, *N*-sodium hydroxide yielded racemic phenylcarbamidoleucine and leucine. F. E. Day.

Colour reactions with lecithin. D. Migliacci Boll. chim. farm., 1928, **67**, 324—325).—The colour reactions obtained on the addition of a concentrated sulphuric acid to a mixture of a 2·5% solution of lecithin in alcohol with a 1% solution of each of the following aldehydes in alcohol is described: furfuraldehyde, benzaldehyde, salicylaldehyde, anisaldehyde, vanillin, and piperonal. E. A. Lunt.

Homogeneity of casein. K. Linderstrøm-Lang (Z. physiol. Chem., 1928, **176**, 76—78).—Casein, prepared from milk by precipitation with dilute hydrochloric acid, washed with water, and dried with alcohol and ether, has been extracted repeatedly with 60% alcoholic 0·001—0·002*N*-hydrochloric acid and the extracts have been treated with sodium hydroxide. The precipitates obtained were washed and dried with alcohol and ether, and these and other fractions have been analysed. Significant differences were observed in the phosphorus content (0·15—1·0%), tryptophan (1·4—2·3%), and tyrosine (3·8—6·1%), with smaller variations in arginine, monoaminodicarboxylic acids, and lysine. Treatment with the acid alcohol did not affect the casein in any way and the whole product is identical physically and chemically with the original preparation. The results indicate a non-homogeneity of casein.

A. Wormall.

Racemisation. VII. Action of alkali on casein. P. A. Levene and L. W. Bass (J. Biol. Chem., 1928, **78**, 145—157).—The mixture of amino-acids obtained by heating casein (4 hrs. at 125° with 5*N*-hydrochloric acid) has α_D^{25} +1·8°; treatment of casein with sodium hydroxide at 25° causes racemisation, the degree of which increases with the time and with the concentration of the alkali; heating at 125° with alkali causes complete racemisation. Casein therefore behaves differently from the polypeptides and diketopiperazines previously investigated, and also from gelatin. It is suggested that casein is composed either of exceptionally stable diketopiperazines or of amino-acids linked in a manner peculiarly favourable to racemisation.

C. R. Harington.

Analysis of mixtures of ethyl alcohol, ethyl acetate, acetic acid, and water. III. Determination of minute quantities of acetic acid. IV. General. S. Poznanski (Rocz. Chem., 1928, **8**, 263—271, 272—274).—A more detailed account of work already published (this vol., 784).

Colorimetric micro-determination of bile salts. O. Coquelet (Compt. rend. Soc. Biol., 1927, **97**, 1815—1818; Chem. Zentr., 1928, i, 1444).—An alcoholic solution (0·5 c.c.) of the pure salt or acid is treated with 1% alcoholic furfuraldehyde solution

(0·1 c.c.), and concentrated sulphuric acid (0·5 c.c.) is added so that the liquids do not mix. A comparison is similarly treated. The contents of the tubes are then rapidly mixed, 5 c.c. of a mixture of chloroform and alcohol (5 : 2) are added, and after 10 min. the tubes are examined colorimetrically. For the determination of bile salts in bile, two or three determinations are made on aliquot portions of a quantity of bile containing 0·5—2 mg. of salts. The bile is rendered alkaline by shaking with ether and 5% sodium hydroxide solution; the aqueous paste is decanted, and dried after being nearly neutralised with oxalic acid. The residue is extracted for 10 min. with chloroform, washed twice with chloroform, and the solution evaporated at a low temperature. The bile salts in an alcoholic solution of the residue are determined as above. Chemical Abstracts.

Determination of morphine in Codex preparations. L. Magendie (Bull. Soc. Pharm. Bordeaux, 1927, **65**, 157—178; Chem. Zentr., 1928, i, 1444—1445).—Denigès' reaction (A., 1911, ii, 79) is applied quantitatively. The chief difficulty is the decolorisation of the solution; this is only partly effected by calcium hydroxide. Instead of copper sulphate solution, a mixture of copper sulphate and hydrochloric acid is employed as catalyst. The method is applied to various pharmaceutical preparations. A. A. Eldridge.

Alkalisation of ash at the expense of alkali chlorides, a source of error in determining organic acids by Hehner's method. P. Fleury and P. Ambert (J. Pharm. Chim., 1928, [viii], **8**, 5—11).—Hehner's method of determining organic acids in the presence of mineral acids uses the conversion by heat of their sodium salts into sodium carbonate which can then be titrated. Contrary to expectation, natural and synthetic gastric juices on incineration gave alkaline ashes. Determinations of the alkalinity of the ash obtained by incinerating in the presence of sodium chloride 21 members of the following groups: amino-acids, proteins, bases, alkaloids, purines, nitrogen-free aliphatic compounds, and nitrogen-free aromatic compounds, indicated that alkalisation with decomposition of sodium chloride occurs chiefly with certain nitrogenous substances, *e.g.*, uric acid, xanthine. It is thought that the substance responsible for the disappearance of hydrochloric acid in the course of incineration itself also disappeared. Hence Hehner's method for determining organic acids in gastric juice is limited to cases where such acids predominate. R. A. Pratt.

Biochemistry.

Hæmocyanin. V. Oxygen dissociation curve of hæmocyanin from the snail (*Helix pomatia*) in dialysed solution. E. Stedman and (Mrs.) E. Stedman (Biochem. J., 1928, **22**, 889—901; cf. A., 1926, 1164; 1927, 689).—The oxygen dissociation curve of hæmocyanin from the snail has been determined at a temperature of 23° and at p_{H} values ranging from 4·04 to 9·04. No detectable change in the curve, which is hyperbolic, was observed with change in p_{H}. It is deduced from the results that one molecule of hæmocyanin combines with one molecule of oxygen and that each molecule of the pigment contains two atoms of copper. Hæmocyanin is molecularly dispersed in solution. S. S. Zilva.

Changes in the oxygen capacity of rabbit's hæmoglobin following partial hepatectomy. B. B. Stimson and M. C. Hrubetz (J. Biol. Chem., 1928, **78**, 413—415).—As in the case of splenectomy (A., 1927, 1217) removal of 75—80% of the liver of rabbits causes conversion of part of the hæmoglobin into a non-oxygen-carrying pigment, not identical with methæmoglobin. C. R. Harington.

Dependence of the catalytic and oxidative actions of iron on its condition of adsorption. R. Kuhn and A. Wassermann (Ber., 1928, **61**, [*B*], 1550—1567).—The ability of hæmin to decompose hydrogen peroxide may be increased to more than 200% by adsorption on animal charcoal. Apart from the initial stages of the reaction, the activity of hæmin is restricted by adsorption by aluminium oxide; metastannic acid, as adsorbent, appears without influence. The transference of oxygen to linseed oil in the presence of hæmin is markedly inhibited by adsorption on charcoal and to a smaller extent by the use of aluminium oxide; metastannic acid exerts practically no influence. Separation of hæmin from the adsorbent is not observed in any case. The results, therefore, appear connected in some manner with the ease of elution of the individual adsorbates. The product when metastannic acid is used, which so closely resembles hæmin in catalytic activity, suffers elution with remarkable ease (2·5% of pyridine suffices), whereas the charcoal and aluminium oxide adsorbates are not thereby changed. Hæmin is removed from aluminium oxide by secondary phosphate, but decomposition of the charcoal adsorbates, in which the catalytic activity is most noticeably altered, cannot be effected.

The products obtained by the adsorption of iron on charcoal show enormously enhanced ability to decompose hydrogen peroxide catalytically, but restricted power of oxygen translation. If the iron is "bedded in" the charcoal (for example, by ignition of a mixture of iron salt and sugar), activation is caused in respect of catalysis and translation. If ferric chloride is adsorbed by aluminium hydroxide, its catalytic activity disappears, whereas great restriction is observed if metastannic acid is used. The opinion is expressed that hydrogen peroxide and ferrous iron can co-exist on charcoal in suitable circumstances. The activation of the catalytic decomposition of hydrogen peroxide by charcoal which has been allowed to adsorb ferric chloride is attributed to reduction to ferrous salt at the bounding surface. If a solution of ferric chloride is shaken with charcoal so that the iron is not quantitatively adsorbed, the liquid, after the adsorbate has been centrifuged, gives a distinct Prussian-blue reaction with potassium ferricyanide. This behaviour has not, however, been observed in the simultaneous presence of hydrogen peroxide. Under these conditions the ferrous iron is present only in the limiting surface, not in solution.

H. Wren.

Transport numbers of fibrin. D. M. Greenberg (J. Biol. Chem., 1928, 78, 265—280).—Determination of the transport numbers of fibrin in dilute solutions of various acids and alkalis indicates that the protein forms completely ionisable salts with alkali hydroxide and with strong acids; in presence of weak acids such as formic, lactic, and phosphoric acids, positively charged ionic complexes of the protein with the acid are formed. The electrochemical equivalent of fibrin, measured by the rate of deposition of the protein on the anode, varied with different methods of preparation.

C. R. Harington.

Precipitation of blood-proteins with tungstic acid. M. Somogyi (J. Lab. Clin. Med., 1927, 12, 800—801).—The blood is preferably added to 8 vols. of 0·09*N*-sulphuric acid; after laking, 1 mol. of 10% sodium tungstate solution is added, the mixture shaken, and filtered after 5 min.

Chemical Abstracts.

Sugars of blood and plasma. Protein-sugar. H. Bierry (Bull. Soc. Chim. biol., 1928, 10, 769—778).—A summary of previous work directing attention to the importance of protein-sugar in glycæmia (A., 1914, i, 218, 346, 454; 1918, ii, 416).

G. A. C. Gough.

Comparison of the Folin–Wu and new Benedict methods for the determination of blood-sugar. A. E. Osterberg (J. Lab. Clin. Med., 1926, 12, 278—282).—Benedict's new method gives lower results than Folin and Wu's method.

Chemical Abstracts.

Ergosterol in human blood. L. H. Dejust, (Mlle.) Van Stolk, and E. Dureuil (Compt. rend., 1928, 187, 311—313).—The unsaponifiable fraction of the fats isolated from human blood-serum shows the three characteristic absorption bands of ergosterol in the ultra-violet region. A further absorption band at a wave-length shorter than 2700 Å. is observed.

G. A. C. Gough.

Cholesterol content of normal human plasma. III. So-called alimentary hypercholesterolæmia. J. A. Gardner and H. Gainsborough (Biochem. J., 1928, 22, 1048—1056).—The level of the cholesterol content of human plasma taken while fasting can be raised or lowered by sufficiently prolonged feeding with diets of high or low sterol content. Such changes are most marked as regards the cholesterol in ester form. As a result of a single meal, alimentary hypercholesterolæmia does not occur and there is no connexion between the amount of sterol ingested and the cholesterol level of the plasma during digestion. As compared with fasting values, the cholesterol content of the plasma fluctuates during digestion. This is probably due to an active endogenous metabolism, in which cholesterol takes part, during the process of digestion. In order to eliminate disturbing factors such as digestion or muscular work, it is important to use for comparative purposes bloods drawn while the subject is in a fasting condition.

S. S. Zilva.

Calcium content of the serum of normal adults. I. Rosen and F. Krasnow (J. Lab. Clin. Med., 1926, 12, 157—158).—The normal value (50 persons) is 10·7—13·2 mg. per 100 c.c.; in no case was less than 10 mg. per 100 c.c. present.

Chemical Abstracts.

Determination of calcium in whole blood. W. R. Caven and A. Cantarow (J. Lab. Clin. Med., 1926, 12, 76—77).—Blood (2 c.c.) is mixed with 4% ammonium oxalate solution (2 c.c.) in a graduated centrifuge tube, and after 1 hr. the mixture is centrifuged at a high speed for 10 min. The supernatant liquid is poured away, the tube inverted on filter-paper for 5 min., the precipitate washed once with distilled water (5 c.c.) and once with dilute ammonia solution (2 vol.-% of concentrated solution; 3 c.c.), and the mat is broken up with a spray of *N*-sulphuric acid (2 c.c.). After being kept at 100° for 1 min. the solution at 75° is titrated with 0·01*N*-permanganate solution.

Chemical Abstracts.

Determination of chlorides in blood or urine. S. L. Lieboff (J. Lab. Clin. Med., 1927, 12, 702—706).—The solution is neutralised with calcium carbonate and titrated with silver nitrate solution, using chromate as indicator; controls are used, and alkaline urine is first acidified.

Chemical Abstracts.

Determination of sodium in blood-serum or -plasma. M. D. Rourke (J. Biol. Chem., 1928, 78, 337—344).—A modification of the method of Kramer and Gittleman (A., 1925, i, 180) is described by which sodium may be determined in 0·3 g. of blood-serum or -plasma with an error of ±2%. The average sodium content of human blood-plasma is 0·339%.

C. R. Harington.

Disappearance of hydrocyanic acid from blood. E. Kohn-Abrest and Lupu (Compt. rend., 1928, 187, 362—364).—"Serum" free from reducing sugars, separated from hog's blood by adding 80 c.c. of 25% trichloroacetic acid per litre of blood, boiling, filtering, and addition of sodium hydroxide, was treated with hydrocyanic acid in the presence and absence of dextrose at 20° and at 37°. In the absence of dextrose there was no loss of hydrocyanic acid in 7 days at 20°; at 37° the loss was 17·2% in 2 days and this figure did not increase in 7 days. In the presence of an amount of dextrose corresponding with that normally present in human blood, 31% of the hydrocyanic acid disappeared in 2 days at 20° and 70% in 4—7 days; at 37° the loss was 68% in 2 days, 71% in 4 days, and 88·5% in 7 days. Similar experiments on the whole blood (with 2% of borax) showed losses of hydrocyanic acid amounting to 7·3%, 10·3%, and 10·8% in 2, 4, and 7 days, respectively, without dextrose, and 14·4%, 24·1%, and 21·1%, respectively, in presence of dextrose at 20°; at 37° the corresponding losses were 7·2, 43·8, and 26·2%, and 31·3, 51·5, and 82·7%, respectively. "Dissimulated" hydrocyanic acid, *i.e.*, as thiocyanate, was detected in the hog's blood at 20° only to the extent of 5% after 7 days at 20°. These results indicate that dextrose is less active in whole blood than in serum, and are not in accordance with the observed absence of hydrocyanic acid from the blood of victims of hydrocyanic acid poisoning. R. Brightman.

Blood stains. P. Karpov (Bull. Univ. Asie Centrale, 1927, No. 16, 152—153).—The stain is extracted with Taraneck's reagent (physiological sodium chloride solution containing 0·25% of sodium carbonate) or Grigoviev's reagent (20% alcohol containing 0·1% of sodium carbonate). In a modification of van Deen's test the solution is mixed with 1—3 drops of guaiacum tincture and 1 drop of ozonised turpentine, and shaken with ammonia solution, which becomes blue. For the microscopical test, the formation of hæmin and hæmochromogen crystals by Bokarius' method is preferred. Halogenohæmatin crystals were best obtained in presence of halogen, chloroform, or iodoform; hæmochromogen crystals were best produced in presence of sodium sulphide and pyridine. Chemical Abstracts.

Benzidine test for blood. K. Scheringa (Pharm. Weekblad, 1928, **65**, 712—713).—The blue colour resulting from the action of oxidising substances on benzidine is produced by hydrogen peroxide only if a catalyst be present. Blood, even at a dilution of 1/10,000, is such a catalyst, as also, however, are numerous inorganic materials, iodides, and, after heating, substances of high protein content; the test is therefore less specific if the material to be tested has been strongly heated. H. F. Gillbe.

Precipitin test for blood. H. S. Shrewsbury (Analyst, 1928, **53**, 380).—It is advisable to test the blood-stain solutions so that they may be within the p_H range for the precipitin reactions, and it was found that rolling the antiserum down the side of the tube inclined at 45° through the solution of the stain gave more definite zone reactions than layering. In Trinidad sera will remain potent only for 3 months even when kept on ice. D. G. Hewer.

Precipitin test for blood. G. R. Lynch (Analyst, 1928, **53**, 435; cf. preceding abstract).—Factors such as temperature during transit, amount of agitation received, age, and other unknown influences render all purchased sera undesirable, and it is considered essential that every worker should make his own sera. D. G. Hewer.

Colloid-chemical significance of electrolytes for precipitation. N. Hayashi (Sei-i-Kwai Med. J., 1927, **46**, 3—5).—Various salts can be substituted for sodium chloride in the agglutination reaction within various limits of concentration. The precipitation is mainly due to the cation, but the anion also has an effect. Chemical Abstracts.

Action of ultra-violet rays on complement. J. Gordon and A. Wormall (Biochem. J., 1928, **22**, 909—919).—Complement of guinea-pig serum is readily inactivated by ultra-violet rays. When the serum is diluted with water or with 0·9% sodium chloride solution the process of inactivation proceeds more readily. This inactivation is primarily due to the inactivation or destruction of the heat-labile components. The relatively heat-stable components are not affected appreciably by irradiation. The separate irradiation of the isolated globulin and albumin fractions produced an inactive complement when recombined. Inactivation in these circumstances was more rapid owing to dilution. This deleterious effect of ultra-violet rays on the activity of the complement is not due to oxidation, although the rate of inactivation in a vacuum is slightly less than that in air. Irradiation of guinea-pigs with ultra-violet rays does not increase appreciably the complement activity of the serum, nor does the serum of guinea-pigs kept in the dark show any marked loss in this activity. S. S. Zilva.

Oxidases and peroxidases of the red bone-marrow, uncombined with hæmoglobin. I. A. Neumann. **II.** A. Neumann and E. Gratzl (Folia Hæmatol., 1927, **35**, 8 pp., 27 pp.; Chem. Zentr., 1928, i, 1198).—I. The term "oxone" is applied to substances which, owing to the presence of oxidases and peroxidases, have the character of a respiratory substance. The preparation of a hæmoglobin-free oxidative substance from the red bone-marrow of the horse, ox, and calf is described. It presumably originates in the leucocyte fraction.

II. The leucocyte value of dogs is increased by the injection of small amounts of "oxone." A. A. Eldridge.

Vital staining of normal and malignant cells. I. Vital staining with trypan-blue and the cytoplasmic inclusions of liver and kidney cells. R. J. Ludford (Proc. Roy. Soc., 1928, **B**, **103**, 288—301).—Dye droplets and mitochondria and dye droplets and Golgi apparatus have been demonstrated in the kidney and liver of animals stained intravitally with trypan-blue. There is no definite relationship between the dye droplets and mitochondria, but the former appear in relationship with the Golgi apparatus, from which they break away into the cytoplasm when formed. It is suggested that products synthesised enzymically at the mitochondrial-cytoplasmic surface diffuse into the cytoplasm and are concentrated at the surface of the Golgi apparatus into droplets preliminary to elimination. S. S. Zilva.

Oöplasmic intermicellar fluid. K. Bialaszewicz (Acta Biol. Exp., Warsaw, 1928, **1**, No. 11, 1—52).—The potassium content of the ash of eggs of birds, amphibiæ, fish, crustacea, molluscs, echinoderms, and annelids is comparatively constant, whilst the sodium, calcium, and magnesium contents, which are considerably lower, are more variable. 20—63% of the volume of the oöplasm is taken up by organic colloidal substances. The greater part of the alkali metals and chlorine present is to be found in the intermicellar fluid in a dialysable form, whilst the alkaline-earth metals and phosphoric acid are for the greater part adsorbed reversibly on the dispersed phase. The mineral content of the intermicellar fluid is fairly constant for the above-named species, 10 parts of sodium, and 7 each of calcium and magnesium being present for every 100 parts of potassium. R. Truszkowski.

Digestibility of white of egg. I. G. Macdonald and E. G. Young (Proc. Nova Scotian Inst. Sci., 1927, **16**, 197).—No difference exists in the rate of peptic digestion of egg-white coagulated for periods of 2—30 min. S. J. Gregg.

Chemical constitution and metabolism of fats in insects. J. Timon-David (Bull. Soc. Chim. biol., 1928, **10**, 784—795).—The oils or fats obtained from insect larvæ exhibit considerable differences in chemical character, some being of the non-drying type, whilst others show a tendency to oxidise in the air. The amounts of oils vary between 3·5 and 27·5% of the body-weight and are least in those larvæ which feed on substances of animal origin. The unsaponifiable fractions vary between 0·75 and 8·5% of the total fats. G. A. C. Gough.

Pigment of the fat of certain rabbits. S. G. Willimott (Biochem. J., 1928, **22**, 1057—1059).—The colouring matter in the adipose tissue of "pigmented" rabbits consists of xanthophyll pigments. S. S. Zilva.

Occurrence of glutathione in the animal kingdom. A. Blanchetière and L. Melon (Compt. rend. Soc. Biol., 1927, **97**, 1231—1232; Chem. Zentr., 1928, i, 709).—A study of cœlenterata, echinoderms, molluscs, annelids, arthropods, and fishes. A. A. Eldridge.

Accumulation of iodine in individual organs. T. von Fellenberg (Mitt. Lebensm. Hyg., 1926, **17**, 235—242).—See A., 1926, 1052.

Iodine metabolism. II. T. von Fellenberg (Mitt. Lebensm. Hyg., 1926, **17**, 223—234).—See A., 1926, 1056.

Colour of the peacock's "eye." (Lord) Rayleigh (Nature, 1928, **122**, 167).—On exposure to the light from a quartz mercury lamp, the dark colour of the centre zone is discharged, whilst that of the second zone is blue in the exposed and green in the unexposed portion. Sunlight has a definite, but less marked, effect. A. A. Eldridge.

Lipase in saliva. K. Scheer (Klin. Woch., 1928, **7**, 163—165; Chem. Zentr., 1928, i, 1428).—Saliva contains a lipase which is destroyed at 65°, and has optimal $p_{\rm H}$ 7. It is activated 300% by calcium chlorate and sodium oleate. A. A. Eldridge.

Thiocyanate content of serum and cerebrospinal fluid. R. Blum (Z. klin. Med., 1928, **107**, 61—71; Chem. Zentr., 1928, i, 1200—1201).—Normal serum contains 0·03—0·06 mg.-% of thiocyanate; smoking increases the value two- to four-fold. Oral administration of thiocyanate caused an increase to, but not above, 1·5 mg.-%. The average value for cerebrospinal fluid is equal to that for serum. A. A. Eldridge.

Organic phosphorus in cerebrospinal fluid. G. E. Youngburg (J. Lab. Clin. Med., 1927, **12**, 845—849).—*Post mortem* change of organic phosphorus is very slow. The organic phosphorus content of cerebrospinal fluid varies from 0·06 to 0·59 mg.%, and is generally 0·1—0·3 mg.%. The phosphorus is not present as lipins, but is probably combined with protein. Organic and inorganic phosphorus contents are independent. Chemical Abstracts.

Differences in chemical constitution, $p_{\rm H}$, and digestive power of pancreatic secretion, according to the nature and intensity of the exciting factor. F. Czubalski (Acta Biol. Exp., Warsaw, 1928, **2**, 1—17).—The chloride content of pancreatic juice is inversely proportional to the velocity of secretion. When secretion is rapid, the $p_{\rm H}$ varies between 8·23 and 8·64, whilst the $p_{\rm H}$ of slowly secreted juice lies between 7·06 and 8·45. These differences are conditioned, not by the nature of the stimulus, but by its intensity. R. Truszkowski.

Mechanism of secretion of calcium and phosphorus in milk. N. C. Wright (J. Agric. Sci., 1928, **18**, 478—485).—In the presence of neutral caseinogenates colloidal calcium hydrogen phosphate is formed by the interaction of calcium chloride and disodium hydrogen phosphate. This colloidal calcium phosphate is non-diffusible across a membrane of cellophane. A mechanism is suggested explanatory of the secretion of high concentrations of calcium and phosphorus in milk from the low concentrations of these elements in the blood. H. J. G. Hines.

Colorimetric determination of free tryptophan in blood. C. A. Cary (J. Biol. Chem., 1928, **78**, 377—398).—Blood is boiled with acetic acid, treated with kaolin, and filtered; the filtrate is treated with sulphuric acid to 7% and the tryptophan precipitated with mercuric sulphate. The precipitate is separated, washed, and suspended in a solution of glyoxylic acid in slightly diluted sulphuric acid. After 48 hrs. at the ordinary temperature the solution is filtered and compared colorimetrically with one obtained by similar treatment of a known solution of tryptophan; a correction must be applied for losses of tryptophan in the process. The colour obtained from blood by this method compares well with that given by pure tryptophan, and tryptophan added to blood can be quantitatively recovered; spectrophotometric analysis, however, indicates that 15—25% of the colour is due to substances other than tryptophan. C. R. Harington.

Free tryptophan in cow's blood and its utilisation in milk secretion. C. A. Cary and E. B. Meigs (J. Biol. Chem., 1928, **78**, 399—407).—The average free tryptophan content of cow's blood is 1·12 mg. per 100 c.c.; the tryptophan content of the blood of the mammary vein is about 17% lower than that of the jugular vein in the lactating cow, whereas in the non-lactating cow the difference is negligible. The proportionate difference in the total amino-nitrogen in the two veins is similar to that between the tryptophan contents. The free tryptophan of the blood appears therefore to be utilised in milk secretion. C. R. Harington.

Urinary elimination of ammonia and nitrogen. Some urinary constants. R. Rafflin (Bull. Soc. Chim. biol., 1928, **10**, 812—821).—Seven equations, describing various functions of the $p_{\rm H}$, the total nitrogen, the ammoniacal nitrogen, and the volume of the urine, are found to give constant values for normal subjects. Large variations are found to accompany pathological conditions and smaller differences occur after sleep and meals. G. A. C. Gough.

Nitrogen excretion of camels. H. W. Smith and H. Silvette (J. Biol. Chem., 1928, **78**, 409—411).—Contrary to the statement of Reid (A., 1925, i, 1204) the camel excretes amounts of carbamide and ammonia comparable with those excreted by other herbivora. C. R. Harington.

Determination of guanidine bases in urine. C. J. Weber (J. Biol. Chem., 1928, 78, 465—473).—Urine is cleared with lead acetate and sodium hydroxide; excess of lead is removed by treatment with sodium phosphate. The filtrate is treated with more sodium hydroxide and the guanidine bases are adsorbed on purified norit; the bases are recovered by treatment of the adsorbate with alcoholic hydrochloric acid, and are then determined colorimetrically by means of a reagent consisting of a mixture of sodium nitroprusside and potassium ferricyanide in alkaline solution. C. R. Harington.

Determination of bismuth in urine. G. Ciogolea (Bul. Soc. Chim. România, 1928, 10, 55—60).—The method of Cuny and Poirot (A., 1923, ii, 792) is most trustworthy for the micro-determination of bismuth. 100 c.c. of urine are evaporated almost to dryness and 2·5—3 g. of ammonium nitrate are added. The residue is ignited and treated with hot water to remove chlorides. The filter-paper used is returned to the dish and incinerated. About 1—1·5 g. of ammonium nitrate, dissolved in the minimum amount of water, is added and, after evaporation, the ignition is repeated. The residue is moistened with a few drops of concentrated nitric acid, evaporated, and again ignited. The resulting ash is dissolved in 4 c.c. of 10% nitric acid, the dish washed with water, and the whole made up to 10 c.c. Bismuth is determined in 5 c.c. of the filtered solution by the colorimetric method of Cuny and Poirot.

J. S. Carter.

Lipins of the blood-plasma in disease. J. Friesz and G. Szabó (Z. klin. Med., 1927, 106, 701—716; Chem. Zentr., 1928, i, 1296).—Changes in the blood-cholesterol and -lecithin in pathological conditions are recorded. In general there is no relation between the blood-cholesterol, -lecithin, and -bilirubin. A. A. Eldridge.

Mineral metabolism. IX. Phosphorus partition of blood in anæmia of cattle and sheep. A. I. Malan (J. Agric. Sci., 1928, 18, 401—405).—In cases of anæmia of cattle and sheep, the nucleoprotein-phosphorus fraction is present and associated with the appearance of nucleated red cells.

H. J. G. Hines.

Calcium and carbohydrate metabolism. Calcium and dextrose tolerance in diabetes mellitus. M. Wishnofsky (J. Lab. Clin. Med., 1927, 13, 133—137).—Intravenous administration of calcium chloride does not appear to influence the tolerance of diabetics for dextrose.

Chemical Abstracts.

Hæmatoporphyrinuria. H. H. van der Z. de Jong (Nederl. Tijds. Geneeskunde, 1928, 72, I, 165—168; Chem. Zentr., 1928, i, 1201)—Part of the porphyrin is present in non-toxic form combined with urofuscin; the name "porfuscin" is given to the compound. It slowly decomposes when the urine is kept, more rapidly when it is heated with dilute hydrochloric acid, producing a dark colour. In congenital porphyrinuria porfuscin is probably not formed. A. A. Eldridge.

Change of the acid–base equilibrium in inflamed tissue. F. Bricker and F. Suponitzkaja (Arch. exp. Path. Pharm., 1928, 133, 103—106).—The acidosis associated with inflammation is a secondary result of the pathological process and not its cause. W. O. Kermack.

Fat, lipin, and cholesterol constituents of adrenals and gonads in cases of mental disease. D. P. Woodhouse (Biochem. J., 1928, 22, 1087—1096)—Analyses of the total alcohol–ether-soluble extractives of the adrenals and gonads of 38 mental patients for total fatty acids, lecithin, sphingomyelin, free and ester cholesterol, and free fatty acids have been performed. The results do not support the view that the lipoids of the gonad are elaborated by and transported directly to it from the adrenal cortex. The percentage of fatty extractives from the gonads shows much less variation than that from the adrenals. The lowest adrenal content was found in dementia præcox and the highest in senile dementia. Low values of phosphatide were obtained in the adrenals of the confusional group and high figures were found in the adrenals of epileptics. The relative proportions of the total cholesterol to the total phosphatide varied greatly in the cases examined and the ratio of these proportions in the pairs of glands differed from unity in a marked degree. S. S. Zilva.

Phosphorus content of serum in renal disease. K. Grassheim and E. Lucas (Z. klin. Med., 1928, 107, 172—180; Chem. Zentr., 1928, i, 1200).—The acid-soluble and organic phosphorus in the serum are normally 2—3·5 and 7—9 mg.-%, respectively. In hot weather the values, particularly the former, are higher. The increase of phosphorus runs parallel with the degree of renal disturbance.

A. A. Eldridge.

Standard for the Van den Bergh test. B. W. Rhamy and P. H. Adams (J. Lab. Clin. Med., 1927, 13, 87—89).—A colour identical with azobilirubin solution equivalent to 5 in 10^6 of bilirubin is given by 0·7 c.c. of 0·1N-potassium permanganate solution diluted to 50 c.c. with water. Chemical Abstracts.

Serum in scarlet fever. E. Tüdös and A. Ebel (Z. ges. exp. Med., 1927, 57, 709—714; Chem. Zentr., 1928, i, 1297).—In scarlet fever the electrolyte content and titratable sodium chloride of the blood-serum are subnormal. A. A. Eldridge.

Increase in blood-sugar in experimental sunstroke of the rabbit. T. Imazu (Proc. Imp. Acad. Tokyo, 1928, 4, 252—253).—The blood of rabbits killed by exposure to the sun had a definitely higher sugar content than before exposure. Those rabbits which survived the exposure showed no hyperglycæmia. J. H. Birkinshaw.

Urinary elimination of iodine and goitre prophylaxis with sea fish. G. Lunde (Ber. int. Kropfkonfer. Bern, 1927, 9 pp.; Chem. Zentr., 1928, i, 1298).—A study of the urinary elimination and intake (in sea fish) of iodine. A. A. Eldridge.

Tissue respiration and endocrine function. I. Influence of thyroidectomy on the phenol oxidase content of animal tissues. II. Influence of thyroparathyroidectomy. J. A. Dye and

R. A. Waggener (Amer. J. Physiol., 1928, **85**, 1—13, 14—20).—I. Observations are reported on the comparative rates of formation of indophenol-blue from dimethyl-*p*-phenylenediamine and α-naphthol in the presence of air and of various tissues from normal and from thyroidectomised lambs and pups. The catalytic system in the tissues is active at 0°, has an optimum at 23—24°, and is destroyed in 30 min. at 55°. The activity of the tissues of animals deprived of their thyroid glands was 50—90% of the corresponding tissues of normal animals.

II. An increase in the oxidase activity of the tissues of the operated animals was found in the case of all the tissues examined except the kidney.

R. K. Cannan.

Sputum. II. H. Müller and H. Reinwein (Z. physiol. Chem., 1928, **176**, 200—206; cf. Reinwein, A., 1926, 1052).—From 2·5 litres of the sputum of a bronchial patient arginine and choline were isolated and identified. Carbamide was not found.

C. Hollins.

Cholesterol content of sputum. R. G. Kelly and M. Pinner (Amer. Rev. Tuberculosis, 1928, **17**, 430—433).—Extensive, acute, and tissue-destructive lesions are associated with an increase in sputum-cholesterol. Chemical Abstracts.

Cerebrospinal fluid in Meningitis tuberculosa. E. Tüdös and A. Ebel (Z. ges. exp. Med., 1927, **57**, 715—720; Chem. Zentr., 1928, i, 1297).—In children the conductivity of the cerebrospinal fluid is normally $1\cdot3\times10^{-2}$ ohm^{-1}; in tubercular meningitis $1\cdot26\times10^{-2}$ ohm^{-1}. That of the serum is $1\cdot08\times10^{-2}$ ohm^{-1}. In meningitis the chlorine content of the fluid progressively diminishes. A. A. Eldridge.

p_H of normal, fœtal, and neoplastic tissues. H. Millet (J. Biol. Chem., 1928, **78**, 281—288).—The p_H of the Flexner rat carcinoma, and of both benign and malignant neoplastic tissue in man, as determined by the glass electrode, is about 6·9, whilst that of the normal tissues is about 7·1; no difference was observed in the p_H of the necrotic and non-necrotic portions of tumours. The p_H of fœtal tissues is low in the early stages of development, but increases steadily and reaches the normal value shortly after birth. C. R. Harington.

Effect of arsenic on some oxidation–reduction systems. G. Barry, E. Bunbury, and E. L. Kennaway (Biochem. J., 1928, **22**, 1102—1111).—Arsenic in the form of arsenite when in concentrations similar to those found in the skin in arsenical hyperkeratosis has a retarding action on the systems (1) hypoxanthine–xanthine oxidase of rat or mouse skin, (2) acetaldehyde–colloidal platinum, and (3) propaldehyde or acetaldehyde, glycine, and phosphate. Arsenates are comparatively inactive in this respect. The possible significance of these findings in connexion with the nature of arsenic cancer is discussed.

S. S. Zilva.

Gaseous metabolism of large wild birds under aviary life. F. G. Benedict and E. L. Fox (Proc. Amer. Phil. Soc., 1927, **66**, 511—534).—The birds examined represent two different heat-producing organisms in which the surface area is without significance. Chemical Abstracts.

Utilisation by the organism of energy liberated by oxidation processes and the food value of alcohol. E. F. Terroine and R. Bonnet (Compt. rend., 1928, **187**, 359—361).—Oxidation processes which take place in the organism are classified according to the utilisation of the energy liberated: (1) those, such as the oxidation of dextrose, in which the energy is used for any kind of work, mechanical or chemical, and (2) those in which the energy can be used only as heat. Alcohol falls into the second class, the energy liberated in its oxidation having no physiological value apart from its thermal effect.

R. Brightman.

Regulation of carbohydrate metabolism. Lactic acid as activator of liver prodiastase. A. Partos (Fermentforsch., 1928, **9**, 403—410).—1·0—1·5 c.c. of 0·7% lactic acid injected intravenously into dogs caused marked hyperglycæmia in 15 min. The assumption that this was due to activation of the liver prodiastase was supported by the observation that the production of dextrose by autolysis of minced liver is inhibited by excess of calcium carbonate or zinc oxide, and proceeds on removal of such excess.

F. E. Day.

Dextrose metabolism of kidney tissue *in vitro*. II. J. T. Irving (Biochem. J., 1928, **22**, 964—967).—Dextrose in phosphate buffer solution containing chopped kidney cortex is converted in large part into lactic acid; a slight fall in the inorganic phosphorus content is observed at the same time. In some cases the fall was sufficient to account for all the dextrose not turned into lactic acid, if it was assumed that hexosediphosphoric acid was formed. In other cases all the dextrose was still not accounted for. This might be due to the formation of a mixture of mono- and di-phosphoric esters. The utilisation of dextrose and the production of lactic acid are strongly inhibited in a vacuum or in the presence of hydrocyanic acid. No glycogen is synthesised by the tissue from the dextrose. S. S. Zilva.

Lactic acid formation in muscle contraction. II. G. Embden and E. Lehnartz (Z. physiol. Chem., 1928, **176**, 231—248).—The values previously obtained (Embden, Lehnartz, and Hentschel, A., 1927, 589) for the quotient (lactic acid excess in nitrogen-muscle)/(lactic acid burnt in oxygen-muscle) are confirmed, using frog's sartorius muscle, these values being much higher than the oxidation quotients of Meyerhof (Pflüger's Arch., 1927, **217**, 549). Certain criticisms by the latter are discussed.

J. H. Birkinshaw.

Pancreatic extracts in relation to lactic acid formation in muscle. E. M. Case and D. R. McCullagh (Biochem. J., 1928, **22**, 1060—1070).—The so-called pancreatic factor which inhibits lactic acid production by muscle enzyme is amylase. It is thermolabile, dialyses through membranes, is adsorbed with difficulty, and is inhibited by the presence of maltose. Its distribution in various animal tissues is also similar to that of amylase. The amylolytic power and the ability to inhibit esterification of phosphates and lactic acid formation correspond in different preparations and are destroyed by heat to the same extent. The presence of different concentrations of starch causes a variation in the inhibiting capacity of the pancreatic factor. Both animal and vegetable amylases act as inhibitors when starch or glycogen is used as substrate. The production of lactic acid from dextrose is not inhibited by the pancreas. The suppression of the esterification of phosphates in the presence of fluoride and starch (cf. McCullagh, this vol., 550) was the technique generally employed in the above experiments.

S. S. Zilva.

Muscular activity. V. Changes and adaptations in running. J. H. Talbot, A. Fölling, L. J. Henderson, D. B. Dill, H. T. Edwards, and R. E. L. Berggren (J. Biol. Chem., 1928, **78**, 445—463).—Figures are given showing the changes in the blood (particularly in relation to respiratory metabolism) and in the urine during periods of work of varying severity in an untrained individual.

C. R. Harington.

Heat of combustion of living muscle. H. Rychlewska (Acta Biol. Exp. Warsaw, 1928, **1**, No. 2, 1—6).—The heat of combustion of 1 g. of fresh frog gastrocnemius muscle is 1076·5 g.-cal.; after drying this value rises to 1094·4 g.-cal. The heat of imbibition of muscle is 12·51 g.-cal. per g. of dry substance. The processes taking place during the drying of muscle must be of an endothermic nature.

R. Truszkowski.

Digestion of lignin by ruminants. F. Rogoziński and M. Starzewska (Acta Biol. Exp. Warsaw, 1928, **1**, [No. 8], 1—9).—Determinations of the methoxy-group content of the fæces of sheep indicates that the lignin contained in oat-straw and that prepared by Beckmann's method (B., 1921, 539) is not digested by these animals and cannot therefore serve as a source of nourishment. R. Truszkowski.

Production of sugar from fat. Y. Kojima (Biochem. Z., 1928, **197**, 31—71).—Rats maintained practically free from carbohydrate with phloridzin could not produce sugar from the fatty acid components of fat. Two such series of rats did not tolerate the daily addition to their diet either of 2·0—4·0 g. of a mixture of 10 g. each of stearic and palmitic acids and 40 g. of oleic acid or of the same amount of the neutralised mixture, and died within 12—24 hrs. Moreover, the addition of 3—4 g. of butter to the diet of four such rats resulted in the average decrease of sugar in the urine of 35·2%, 19·3%, 11·8%, and 20·7%, showing that the formation of sugar from the glycerol of the fat was completely suppressed, the fatty acids of the fat being responsible for this marked inhibition. Comparison of the sugar in the urine of such rats fed on meat, fat, and a mixture of the two showed an excess of excreted sugar of 54% for flesh over fat, of 38% for flesh plus fat over fat, and of 26% for flesh over flesh plus fat. The excretion of sugar on a feeding day exceeds that on a starving day, for meat by 50% and for fat by 14·4%. Finally, the addition of 1 g. of sodium lactate to the diet of three rats resulted in an average increase of sugar production of 34·8%. L. C. Baker.

Conversion of fat into carbohydrate. I. Metabolism of acetic acid. H. J. Deuel, jun., and A. T. Milhorat (J. Biol. Chem., 1928, **78**, 299—309).—After injection of sodium acetate into phloridzinised dogs the acetic acid was almost completely oxidised, but no significant change in the D : N ratio took place. Acetic acid cannot therefore readily give rise to dextrose, and this is further evidence against the supposed formation of carbohydrate from fat in the animal organism. C. R. Harington.

Lipin and fat metabolism during fattening. H. Knauer (Z. physiol. Chem., 1928, **176**, 151—172).—Plasma, serum, and erythrocyte fractions of blood from pigs slaughtered at various stages of fattening were analysed for phosphatides, cholesterol, and fatty acids. The lipin values of the pig are comparatively low; there is a definite decrease of all lipins during fattening, those of serum showing the greatest change and those of the erythrocytes the least. The rate of settling of the blood-corpuscles diminishes progressively.

In the case of geese, there is a similar steady decline in the lipins with increasing body-weight; when the fattening is intensive, the lipin values fall while fat is being accumulated, but rise considerably when weight equilibrium is reached. J. H. Birkinshaw.

Chemical composition of eels subjected to inanition. T. Vieweger (Acta Biol. Exp., Warsaw, 1928, **1**, No. 10, 1—19).—Eels weighing from 300 to 700 g. have a solid content of 50%, a nitrogen content of 2·35%, and a fatty acid content of 27·5%. Proteins represent 31·5% of the organic content, and fats 68·5%. Most of this fat is in the muscles and the adjacent subcutaneous layer, the skin and viscera accounting for only about 7% of the total fat content. After a period of inanition lasting up to 320 days and involving a loss of weight of up to 26%, the relative proportions of the organic constituents of these animals remain unchanged, indicating that no biological constituent is preferentially consumed under the above conditions. R. Truszkowski.

Formation of organic bases during incubation of eggs. Y. Nakamura (Z. physiol. Chem., 1928, **177**, 34—41).—The free choline of hen's eggs is present only in the yolk. The quantity, originally 0·64 mg. per egg, decreases and reaches a minimum after 9 days' incubation; it then increases both in the yolk and in the embryo, reaching 2·27 mg. after 19 days. Combined choline is present in much greater amount and reaches a maximum (93·34 mg.) after 9 days, falling to 29·54 mg. at the 19th day. The increase in free choline is doubtless due to hydrolysis of combined choline, but most of the lecithin must undergo some other change, possibly into creatinine.

C. Hollins.

Cause of the specific dynamic action of albumin. II. III. R. Liebeschütz-Plaut and H. Schadow (Pflüger's Archiv, 1927, **217**, 717—722, 723—727; Chem. Zentr., 1928, i, 714).—Following intravenous administration of amino-acids the usual specific dynamic effect is not observed. In intraduodenal administration of glycine the oxygen-consumption curve follows the blood-amino-nitrogen curve. A. A. Eldridge.

Nutrition. I. Growth, reproduction, and lactation on diets with different proportions of cereals and vegetables. II. Effect of addition

of egg. M. S. Rose and E. L. McCollum (J. Biol. Chem., 1928, **78**, 535—547, 549—555).—I. Diets devised to imitate those consumed by normal children, ranging in the proportion of cereal (flour) and vegetables, were found adequate for growth and reproduction in rats, but lactation was unsatisfactory, owing, possibly, to deficiency in vitamin-*B*.

II. Addition of egg to such a diet caused improvement in growth of the young, fertility of the females, and lactation. C. R. Harington.

Mineral metabolism. IV. Determinations of phosphorus compounds in blood by dry combustion. H. H. Green (J. Agric. Sci., 1928, **18**, 372—375).—Dry combustion is combined with the coeruleomolybdate procedure of Denigès.

H. J. G. Hines.

Mineral metabolism. V. Composition of bovine blood on phosphorus-deficient pasture. A. I. Malan, H. H. Green, and P. J. du Toit (J. Agric. Sci., 1928, **18**, 376—383).—Examination of the phosphorus partition of the blood of cattle grazing on phosphorus-deficient pasture of South Africa showed that the outstanding characteristic is low inorganic phosphorus with a correlated reduction in total phosphorus. When a small ration of bone meal is given to the animals, comparatively normal figures are obtained. Colorimetric determination of inorganic phosphorus in the blood of the grazing animal provides a simple means of detecting deficiency in the pasture.

H. J. G. Hines.

Mineral metabolism. VI. Comparison of the blood of the cow and calf in respect to mineral constituents. H. H. Green and E. H. Macaskill (J. Agric. Sci., 1928, **18**, 384—390).—Total phosphorus of the blood of the new-born calf may be twice that of its mother. The red corpuscles contain all the organic acid-soluble phosphorus in both calf and cow, and in the case of the calf they contain also an unknown phosphorus fraction, probably of nuclear origin. An outstanding feature of calf blood is its high potassium content. H. J. G. Hines.

Mineral metabolism. VII. The unknown phosphorus fraction of calf blood. A. I. Malan and H. H. Green (J. Agric. Sci., 1928, **18**, 391—395).—This fraction is shown to be nucleoprotein and due to the presence of precursors of fully mature erythrocytes. This fraction may occur in small amounts in human and horse blood and always occurs in very large amount in the nucleated erythrocytes of birds. H. J. G. Hines.

Mineral metabolism. VIII. Comparison of phosphorus partition in the blood of calf fœtus, sheep fœtus, and lambs with corresponding maternal blood. A. I. Malan (J. Agric. Sci., 1928, **18**, 397—400).—A similar phosphorus partition in the blood of ewes and lambs to that obtaining in cows and calves was observed. H. J. G. Hines.

Normal deposition of mineral in the bones of dairy calves. J. H. Kruger and S. I. Bechdel (J. Dairy Sci., 1928, **11**, 24—34).—The phosphorus and calcium content of the bones of male calves at 90—180 days was constant; water decreased, whilst fat, ash, and organic matter increased, with age.

Chemical Abstracts.

Calcium fixation capacity of normal and rachitic cartilage. W. Schmidt (Z. Biol., 1928, **87**, 537—542).—The following specimens were examined for calcium fixation by placing the tissues in a calcium chloride solution for 24 hrs. Calf's epiphysis, cattle rib cartilage, cattle shoulder cartilage, proliferating and non-proliferating zones of calf's rib cartilage, rachitic and non-rachitic cartilage from children, and proliferating and non-proliferating zones of cartilage from rachitic children. There is no relationship between calcification and calcium fixation of these tissues. S. S. Zilva.

Biological significance of salt concentration in natural waters. C. Schlieper (Naturwiss., 1928, **16**, 229—237).—Both the number and the size of many marine animals decrease in regions where the salt concentration is less than that of the open sea. This is partly due to the difference in osmotic pressure between the body fluid and the external solution. In many cases the breathing apparatus of fresh-water animals is larger than that of closely related marine animals. It is suggested that the greater capacity for absorption of carbon dioxide possessed by sea-water is the reason why breathing is easier in sea-water than in fresh water. Rise of temperature increases the combination of carbon dioxide, and this explains why certain marine animals thrive in fresh water in warm climates. The effect of the carbonate/hydrogen carbonate equilibrium on the distribution of plankton is discussed. W. A. Richardson.

Oxidation of luciferin without luciferase; mechanism of bio-luminescence. E. N. Harvey (J. Biol. Chem., 1928, **78**, 369—375).—Luciferin in aqueous solution can be oxidised by a variety of oxidising agents, but in no case is luminescence produced unless luciferase be present; an alcoholic solution of luciferin luminesces slightly when heated or on treatment with certain oxidising agents. The presence of oxidising luciferin alone or of luciferase alone does not cause fluorescent dyes to luminesce, nor is luminescence shown by a solution of luciferase in electrical contact with one of luciferin. The previous hypothesis, that luminescence is due to activation of the luciferase molecules in the process of oxidising luciferin, is therefore confirmed.

C. R. Harington.

Salt action and diuresis. E. Bloch (Z. klin. Med., 1927, **106**, 733—744; Chem. Zentr., 1928, i, 1298).—A study of the elimination of salts after simultaneous administration of water and intravenous injection of potassium chloride.

A. A. Eldridge.

Phosphorus and calcium in blood after injection of brewer's yeast. C. I. Urechia and G. Popoviciu (Compt. rend. Soc. Biol., 1927, **97**, 1009—1011; Chem. Zentr., 1928, i, 371).—Injection of brewer's yeast causes fever; during rigor the phosphorus and calcium content of the blood is increased, falling to normal values during the fever.

A. A. Eldridge.

Pharmacological studies of the sterols. H. Seel (Arch. exp. Path. Pharm., 1928, **133**, 129—180).—The substances were employed in the non-irradiated as well as in the irradiated condition and colloidal aqueous solutions were used. Oxycholesterol, which always accompanies cholesterol in the animal organism, was specially considered. All the sterols and derivatives used powerfully stimulated the activity of the normal isolated frog heart and oxycholesterol had the strongest effect. Fatigued and also injured (poisoned) frogs' hearts were frequently restored to normal by these sterols. Irradiation of the compounds by "artificial sunlight," except in a few cases where there was slight increase of stimulating effect on the heart, had scarcely any influence on that effect. The action of sterols on the heart is a specific effect, although adsorption phenomena may also be involved. The sterols, particularly oxycholesterol and oxysitosterol, acted powerfully on the smooth muscle of the uterus, raising the tonus and stimulating contraction. These sterols antagonised the influence of adrenaline on the activity of the uterus; they had only slight effect on the blood pressure. Oxycholesterol had a beneficial influence on metabolism and on growth. The oxygen requirements of rats were raised by it; the growth of their hair and the condition of their skin were greatly improved. Unirradiated oxycholesterol and oxysitosterol blackened the photographic plate, but the view that the photographic effect is related to antirachitic and antixerophthalmic properties could not be confirmed. Of the substances used, even when irradiated, only irradiated cholesterol had antirachitic effects. Unirradiated oxycholesterol prevented xerophthalmia, cured it in its initial stages, and favourably modified its effects in advanced stages. In "avitasterolosis"-*A* and -*D* there was a limitation of the oxidations in the organism. In xerophthalmia the diminution of the basal metabolic rate ran parallel with the retardation or stoppage of growth, but in rickets the limitation of oxygen consumption reached a much greater value than would correspond with the loss of weight.

W. McCartney.

[Action of] animal poisons [on lecithins and lysocithins]. A. Contardi and P. Latzer (Biochem. Z., 1928, 197, 222—236).—The hæmolytic power of lysocithin prepared from egg yolk by the action of cobra venom was found to be slight at a dilution of 1/20,000, strong at 1/18,000, whilst that of its double salt with cadmium chloride was slight at 1/20,000, but strong at 1/15,000; of lysocithin–cadmium chloride prepared from lecithin from pancreas slight at 1/4000, strong at 1/2000, and obtained from brain slight at 1/6000 and strong at 1/5000. Wasp poison decomposed both lecithin– and lysocithin–cadmium chloride to cadmium chloride, glycerol, phosphoric acid, fatty acids, and choline; the lipase of castor seed acted similarly, but with octahydroanthracenesulphonic acid ("idrapid") a lysocithin was obtained which was strongly hæmolytic at a dilution of 1/4000, before undergoing similar decomposition. Calcium and sodium glycerophosphates were decomposed to give phosphoric acid by wasp poison and "idrapid," but not by cobra or bee poison or castor-seed lipase. Bee, cobra, and wasp poison and castor-seed lipase did not attack phytin. The nature of the fatty acids of lecithin was investigated by determining iodine values.

L. C. Baker.

Guanidine. II. Distribution of guanidines in acute guanidine and parathyroprivia tetanies. III. Water content of certain tissues during acute guanidine and parathyroprivia tetanies. IV. Changes in guanidine action and in parathyroprivia tetany produced by dextrose. M. M. Ellis (Biochem. J., 1928, 22, 930—936, 937—940, 941—946).—II. Analyses of blood, voluntary muscle, liver, kidney, and brain of rabbits in acute guanidine tetany and in acute phenol tetany were made and compared with those of normal animals for guanidine and creatine content. The guanidine contents of the livers, kidneys, and brains of animals in acute guanidine tetany were high, whilst those of the blood and muscle even at the point of death were lower than in normal animals. There were relatively large amounts of guanidine in the brain of the guanidine tetany animals. No storage of guanidine was observed. The guanidine content of the brain of the untreated cat in acute parathyroprivia tetany is relatively high.

III. Brain, kidney, and striated muscle from animals (rabbit, cat, frog, and rat) in acute guanidine and parathyroprivia tetanies have a higher water content than the same tissues from normal animals. The ash : solids ratio in the respective tissues of both cases is, however, the same. Blood from rats in acute guanidine tetany has a lower water content than normal rat blood.

IV. From experiments on frogs it was found that dextrose–guanidine is less active both chemically and biologically than its equivalent of guanidine base. Combined injections of dextrose and guanidine carbonate are less toxic than injections of guanidine carbonate alone. Parathyroprivia tetany in cats is relieved by means of dextrose and adrenaline injections.

S. S. Zilva.

Chemical constitution and pharmacological properties of the methylglyoxalines. I. J. V. Supniewski (Acta Biol. Exp. Warsaw, 1928, 1, No. 9, 1—19).—4-Methylglyoxaline has a depressor action, is a strong diuretic, and produces contractions in the isolated guinea-pig's uterus, but not of an intestinal loop. 2-Thion-4-methylglyoxaline and glyoxaline-4-carboxylic and -4 : 5-dicarboxylic acids are pharmacologically inactive, as is 4-hydroxymethylglyoxaline, except that the latter excites uterine and intestinal contractions. 5-Methyl-4-hydroxymethylglyoxaline has an action similar to that of methylglyoxaline. 4-Chloromethylglyoxaline has a powerful depressor action, inhibits the isolated frog's heart, and produces uterine contraction. 4-Aminomethylglyoxaline has an action similar to that of histamine, although weaker. 2-Thion-4-aminomethylglyoxaline has a feeble depressor action, and a slight inhibitive action on cardiac muscle. 4-Diethylaminomethylglyoxaline has an oxytocic and peristaltic action, inhibits the action of the heart, has an intense depressor action, and enhances both the rate and the amplitude of respiration. 4-Piperidylmethylglyoxaline is a powerful depressor, a cardiac inhibitor, a powerful diuretic, and an oxytocic agent, whilst having no action on other non-striated muscles.

R. Truszkowski.

Metabolism of animals after [administration of] synthalin. A. Moschini (Compt. rend. Soc.

Biol., 1927, 97, 1199—1201; Chem. Zentr., 1928, i, 713).—The influence of synthalin on metabolism differs from that of insulin. Small doses (up to 2 mg. per kg.) of synthalin raise the blood-sugar; the hypoglycæmia following large doses (2·5—3 mg. per kg.), but not the other toxic symptoms, is affected by administration of dextrose. A. A. Eldridge.

Hypoglycæmic properties of galegine sulphate. H. Simonnet and G. Tanret (Bull. Soc. Chim. biol., 1928, **10**, 796—805).—See this vol., 199.

Action of some convulsion-producing poisons on blood-sugar, lactic acid, and alkali reserve. I. Fujii (Arch. exp. Path. Pharm., 1928, **133**, 242—256).—The substances used (picrotoxin and the sodium derivative of santonin) increase blood-lactic acid in two ways: If convulsions occur increased muscular activity leads to increase of lactic acid without change in the amount of blood-sugar. Without or before convulsions there is a second form of lactic acid increase which runs parallel with an increase in blood-sugar. These actions on lactic acid and blood-sugar are centrally conditioned and depend on the intactness of the splanchnic nerve. A connexion with adrenaline secretion may be assumed as far as increase of blood-lactic acid and of blood-sugar is concerned, for adrenaline produces simultaneous increases of both substances. Increase of lactic acid and consequent lowering of alkali reserve results in increased tendency to convulsions. If this lowering is prevented by section of the splanchnic nerve or if alkali is supplied the minimal dose required to produce spasms is raised not inconsiderably. Experiments with guanidine were inconclusive, but it seems that the convulsions produced by it are not analogous to those caused by insulin. W. McCartney.

Chronic morphine poisoning in dogs. I. General symptoms and behaviour during addiction and withdrawal. O. H. Plant and I. H. Pierce. **II. Changes in blood cells and hæmoglobin during addiction and withdrawal. III. Blood-sugar during tolerance and withdrawal.** J. H. Pierce and O. H. Plant (J. Pharm. Exp. Ther., 1928, **33**, 329—357, 359—370, 371—385).

Accumulation of arsenic in the brain following administration of neosalvarsan, arsenious and arsenic acids. B. Engelmann (Arch. exp. Path. Pharm., 1928, **133**, 181—191).—After intravenous injection of neosalvarsan a fairly definite accumulation of arsenic in the brain was observed, provided injections were continued for several weeks. When dextrose was injected at the same time as neosalvarsan increased amounts of arsenic accumulated in the brain. Considerable increase also took place when the drug was administered during fever. When injections were given during urethane narcosis there was partial or total suppression of the normal capability of the brain to accumulate arsenic. Deep ether narcosis acted similarly. The brain did not take up increased amounts of arsenic when the injections were preceded by administration of substances such as amyl nitrite, caffeine, and theophylline nor, apparently, in acute meningitis. Sodium arsenite and sodium arsenate when injected alone had effects similar to those produced by neosalvarsan alone. Rabbits were used, but the neosalvarsan was administered under conditions as similar as possible to those used for human beings. Arsenic was determined in the brain by Lockemann's modification of the method of Marsh and the determinations were checked, where possible, by Bang's process (A., 1926, 39). W. McCartney.

Toxicology of lead and its compounds. IV. Electrolytic detection of lead. V. Nephelometric determination of lead. P. W. Danckwortt and E. Jurgens.—See this vol., 981.

Urinary hæmatoporphyrin excretion in chronic lead poisoning. S. Hirschhorn and W. Robitschek (Z. klin. Med., 1927, **106**, 664—670; Chem. Zentr., 1928, i, 1298).—Hæmatoporphyrinuria, in which the spectrum of acid hæmatoporphyrin is visible with a 5 cm. layer of unacidified urine, is pathological; this was observed in 6 of 77 cases of lead poisoning. There is a close connexion between the disintegration of erythrocytes and the production of hæmatoporphyrin. A. A. Eldridge.

Similarities in the catalytic action of enzymes and of definite organic substances. W. Langenbeck (Z. angew. Chem., 1928, **41**, 740—745).—A review. A. Davidson.

Toxic action of nascent tellurium and selenium on enzymes. R. Labes (Arch. exp. Path. Pharm., 1928, **133**, 57—62).—When saliva is incubated with hydrazine hydrate and telluric acid, the tellurium which is formed in a finely-divided condition is flocculated and at the same time the diastatic action of the saliva is destroyed. Hydrazine and telluric acid separately are without action, and if sufficient mucin is present so that precipitation of the colloidal tellurium does not occur, the diastase is not inactivated. It therefore appears that in order that inactivation should take place the nascent tellurium particles must come into direct contact with the enzyme. Nascent selenium behaves similarly. W. O. Kermack.

Development of mutase action in germinating barley. Z. I. Kertész (Z. physiol. Chem., 1928, **176**, 144—150).—The enzymic mutation of acetaldehyde by germinating barley was found to vary directly with the time of germination. The mutase action decreased in the rootlets and increased in the shoots from the 12th to the 18th day. In comparative experiments with yeast, reaction coefficients showed no constancy, but a definite relation existed between the amount of yeast and the mutase action.

J. H. Birkinshaw.

Rôle of hexosemonophosphate in enzymic degradation of sugar. H. von Euler and K. Myrbäck (Annalen, 1928, **464**, 56—69).—The mechanism of the fermentation of dextrose is probably as follows: (1) Under the influence of a synthetic enzyme, phosphatese, Robison's hexosemonophosphate (A., 1923, i, 86) is formed, but no free phosphate or carbon dioxide appears. (2) The monophosphate, under the influence of a "mutase" and the co-zymase, undergoes conversion, half into alcohol and carbon dioxide, and half into hexosediphosphate. (3) The latter is converted by a phosphatase into a hexose (lævulose ?), which (4) enters into the chain of processes given above. The velocity of fermentation of monophosphate by dried yeast is the same as that of a mixture of equivalent quantities of dextrose and phosphate.

A method is described for the determination of mono- and di-phosphate during the course of fermentation (cf. Harden and Henley, A., 1927, 1113).

Most preparations of dextrose monophosphate using dried yeast give a product with $[\alpha]_D$ about $+26°$ (barium salt $+13°$), but when a very strongly phosphatising yeast was used, the product had $[\alpha]_D$ $+63°$ and is probably distinct from Robison's material.

E. E. Turner.

Occurrence and decomposition of pyrophosphate in muscle. K. Lohmann (Naturwiss., 1928, **16**, 298).—The increase of phosphate on digestion of muscle with sodium hydrogen carbonate solution is ascribed chiefly to enzymic hydrolysis of pyrophosphate to dipotassium hydrogen orthophosphate, and not to decomposition of lactacidogen.

Chemical Abstracts.

Dehydrogenation of malic acid. I. A. Hahn and W. Haarmann (Z. Biol., 1928, **87**, 465—471).—In the presence of washed muscle reduction of methylene-blue is brought about by malic acid and the formation of carbon dioxide is also observed. The liberation of carbon dioxide appears to occur subsequent to the reduction of methylene-blue and it is suggested that by the dehydrogenation of malic acid oxalacetic acid is formed and that this compound then liberates carbon dioxide at a rate accelerated by the presence of the muscle tissue.

W. O. Kermack.

Enzymic decomposition of starch. K. Sjöberg (Fermentforsch., 1928, **9**, 329—335).—A review.

F. E. Day.

Lipase of the larva of *Galleria mellonella*. V. Pertzov (Compt. rend., 1928, **187**, 253—255).—In solutions of p_H 8·2 (± 1) and at 37—45°, the lipase of the larva hydrolyses emulsions of olive oil and of beeswax. The fat of tubercle bacilli, killed by heat, is also hydrolysed at 45°, with formation of acids. The lipase or lipases are equally soluble in 50% glycerol, *N*-sodium chloride solution, and in water made alkaline with ammonia. The presence of ethyl alcohol stops the action of the lipase. The extracts did not completely destroy living tubercle bacilli but produced very characteristic changes, the bacilli forming granules and losing their acid-fastness.

R. Brightman.

Rennin coagulation of milk. Effect of hirudin, heparin, kephalin, and removal of fat. J. B. Stone and C. L. Alsberg (J. Biol. Chem., 1928, **78**, 557—572).—Hirudin and kephalin were without effect on the coagulation of milk by rennin; various preparations of heparin, similar as regards their effect on blood coagulation, were variable in their effect on milk clotting. Extraction of a rennin solution with ether did not impair its coagulating properties. The presence of large amounts of ether, alcohol, or chloroform inhibits coagulation, whilst benzene, light petroleum, and saponin have little effect; soap solution delays coagulation, but the effect is neutralised by simultaneous addition of calcium chloride, and is probably due to precipitation of calcium. Milk skimmed in the centrifuge coagulates more slowly than milk skimmed by gravity; this may be partly due to the violent agitation of the milk in the former case.

C. R. Harington.

Conductivity method and proteolysis. II. Interpretation of conductivity changes. H. D. Baernstein (J. Biol. Chem., 1928, **78**, 481—493; cf. A., 1927, 992).—At p_H 1·4 or less the rate of change of conductivity of a peptic digest of egg-albumin is coincident with the rate of change of amino-nitrogen; at more alkaline reactions there is divergence between the two. The change of conductivity calculated from the change in p_H is greater than the observed change when the conductivity is decreasing, and less when it is increasing; the discrepancy is to be ascribed to the dicarboxylic acids, since a similar phenomenon is observed on addition of glutamic or aspartic acid to a solution of hydrochloric acid, whilst on addition of glycine to such a solution the observed and calculated changes in conductivity show good agreement. It appears that the binding of hydrogen ions by amino-acids which takes place during peptic digestion is explicable on Bjerrum's theory (A., 1923, i, **444**) of ampholytic dissociation. C. R. Harington.

Action of pepsin of herbivora and carnivora on vegetable and animal proteins. H. W. Vahlteich (Z. physiol. Chem., 1928, **176**, 222—230).—No differences were observed in the digestion of various proteins by the pepsin derived from the horse and that from the dog. The number of carboxyl groups set free, determined by Willstätter's method, was consistently higher than the number of amino-groups determined according to Van Slyke; the ratio $CO_2H : NH_2$ varied according to the protein used.

J. H. Birkinshaw.

Alcohol. VI. Influence of alcohol on the action of pepsin. G. Franzen (Arch. exp. Path. Pharm., 1928, **133**, 111—120).—Up to concentrations of about 11%, ethyl alcohol promotes the proteolytic action of pepsin *in vitro*, but at higher concentrations it is inhibiting. White wine, red wine, and beer have a favourable effect on the activity of pepsin approximately corresponding with their content in ethyl alcohol, but this effect is most marked in the case of white wine. It appears to be partly neutralised in the case of beer by its action on the acid present in the digestion mixture and in the case of red wine by its content of tannic acid. W. O. Kermack.

Peptidases. H. von Euler and Z. I. Kertécz (Ber., 1928, **61**, [*B*], 1525—1529).—Fission of glycylglycine by a glycerol extract of pig intestine is greatly hindered by alcohol, boric acid, aniline, or glycine, but the effect of ethyl aminoacetate could not be investigated owing to the presence of lipase in the enzyme mixture. The effect of quinine sulphate or quinidine sulphate is not marked. Ammonia is without influence. The fission of alanylglycine is inhibited by glycine. H. Wren.

Determination of trypsin in pancreatic juice. B. Goldstein (Fermentforsch., 1928, **9**, 322—328).—The Fuld–Gross method is modified by taking the first appearance of tryptophan as the end-point, instead of the absence of casein precipitate on acidifying. F. E. Day.

Effect of acidity and boiling on enterokinase. I. P. Rasenkow (Fermentforsch., 1928, 9, 382—388).—Working with material obtained from dogs it is found that 0·5% hydrochloric acid has no harmful effect on enterokinase, which can activate pancreatic secretion in presence of 0·3% of hydrochloric acid. Boiling destroys the activating power of enterokinase in neutral but not in such acid solutions.

F. E. Day.

Influence of thyroxine, 3 : 5-di-iodotyrosine, and thyroid-substance on the course of autolysis and on the action of erepsin and trypsin. E. Abderhalden and K. Franke (Fermentforsch., 1928, 9, 485—493).—The autolysis of 35—45 g. of pulped liver with 100 c.c. of water and 50 c.c. of phosphate buffer, p_H 8, is retarded by 1 mg. of thyroxine, but accelerated by 0·01 mg. and even by 0·001 mg. 3 : 5-Di-iodotyrosine and thyroid behave similarly, but not in proportion to their iodine content. The effect appears to be to some extent affected by the reaction of the medium. Similar results are obtained as regards the action of pancreas extract and erepsin on *dl*-leucylglycine and of trypsin-kinase on peptone and gelatin, although to a much less marked degree.

F. E. Day.

Kinetics of the tyrosinase of potatoes. H. Haehn and J. Stern (Fermentforsch., 1928, 9, 395—402).—The course of the oxidation of tyrosine under the influence of tyrosinase is unimolecular in presence of excess of oxygen. The coefficient is dependent on the concentration of the enzyme, not on that of the tyrosine. The ratio K/(weight of enzyme preparation) is therefore a measure of activity.

F. E. Day.

Tyramine oxidase. I. An enzyme system in liver. M. L. C. Hare (Biochem. J., 1928, 22, 968—979).—A cell-free extract of liver is described which is capable of oxidising *p*-hydroxyphenylethylamine, one atom of oxygen being taken up per molecule of tyramine. Hydrogen peroxide is produced during the reaction, whilst methylene-blue is not reduced. The oxidation is not affected by the addition of 0·002M-potassium cyanide. Deamination of the compound occurs simultaneously, but only half the nitrogen in the tyramine molecule is accounted for as ammonia. The optimum reaction of the system is at p_H 10·0. The enzyme is inactive but not destroyed at p_H 4·4, but destruction occurs at p_H 11·5. Phenylethylamine and possibly also *p*-aminophenol are oxidised by the enzyme, but tyrosine and many other substances are not attacked. The enzyme is distinct from tyrosinase. The oxygen uptake was measured by the Barcroft differential manometer.

S. S. Zilva.

Glycocyamase. J. Karashima (Z. physiol. Chem., 1928, 177, 42—46).—Ox-liver preparations contain glycocyamase, since they convert guanidinoacetic acid into carbamide and glycine. The enzyme is absent from kidney, pancreas, spleen, and lung of cattle, and from liver and kidney of hens.

C. Hollins.

Specific action of salts in extraction of urease from amœbocytes of *Limulus*. L. Loeb, I. Lorberblatt, and M. E. Field (J. Biol. Chem., 1928, 78, 417—431).—Magnesium and manganese chlorides show, in a smaller degree, the favourable effect previously observed (A., 1927, 484) for the salts of the alkaline earths in the extraction of urease; tervalent ions, on the other hand, have little or no effect on the extraction. Those salts which, in dilute solution, are most efficient in extracting urease are, in higher concentration, most toxic to the enzyme. An optimal extraction of the enzyme by sodium chloride solution is obtained in presence of 0·005N-sodium hydroxide and of 0·0005N-hydrochloric acid. Addition of calcium chloride to a sodium chloride extract does not affect the activity, but its addition to a magnesium chloride extract increases the activity in proportion to the calcium chloride added. Extractions with mixtures of salts give results intermediate between those obtained with the pure salts. It appears that the interactions of urease with salts may be divided into non-specific effects, *e.g.*, the injurious action of the heavy metals and osmotic effects, and specific effects consisting of formation of compounds with various cations; of these compounds, those with the alkaline earths are the most active, and those with the alkali metals are irreversible in character.

C. R. Harington.

Influence of structure on the kinetics of desmolases. I. Systems uricase–uric acid–active and inactive charcoal or protein. S. J. Przyłecki (Acta Biol. Exp. Warsaw, 1928, 1, No. 6, 1—26).—Uric acid and uricase are strongly adsorbed on iron-free charcoal, from which the former substance may to a great extent be eluted by the addition of alcohols. Adsorption does not inactivate uricase, but simultaneous adsorption of uric acid and uricase leads to a reduction in the total quantity of uric acid decomposed, although the percentage of that oxidised in solution, as opposed to that present in the system as a whole, is the same whether charcoal is present or not. Oxidation of uric acid is in all cases proportional to its concentration in solution, and for this reason is enhanced by the addition of elutive agents. Where active animal charcoal is used, both enzymic and catalytic oxidations occur; the action of these two factors is, however, independent, so that if allowance be made for the quantity of uric acid oxidised through the agency of the charcoal, the results obtained are similar to those of the first system. Restriction of access of oxygen does not affect these results. Coagulated egg-white has a very feeble adsorptive action on uric acid, but adsorbs uricase very strongly. Since simultaneous adsorption does not take place, the introduction of this adsorbent does not sensibly retard the reaction of uricolysis, and the same applies to soluble egg-white.

R. Truszkowski.

Uricase and its action. I. Preparation. S. J. Przyłecki (Biochem. J., 1928, 22, 1026—1034).—Frogs were ground, extracted with a mixture of water, chloroform, and glycerol, and the extract was precipitated with acetone. The precipitate when dissolved in a volume of 1% salt solution which was equivalent to the original volume of the glycerol extract yielded a solution more active than the original extract. This extract can be further purified by dialysis, ultra-filtration, or reprecipitation with alcohol or by a mixture of alcohol and acetone.

Uricase preparations from mammalian kidney and from wheat-seed were similarly prepared.
S. S. Zilva.

Wildier's bios. Isolation and identification of "bios I." (Miss) E. V. Eastcott (J. Physical Chem., 1928, **32**, 1094—1111; cf. Tanner, Chem. Reviews, 1924, **1**, 399).—The crops of yeast obtained under standard conditions from 48 vegetable and 15 animal preparations are compared with those obtained by adding bios I or II (prepared from malt combings) or wort to the extracts. The results indicate that all the extracts examined contain bios I and II which are physiologically identical with those prepared from malt-combings. Bios I has been isolated from tea dust and is identical with *i*-inositol. The curves showing the rate of reproduction of yeast in solutions containing salts, sugar, inositol, and crude bios II have the same form as those obtained by Clark (A., 1922, i, 501) with solutions of salts, sugar, and wort. The inositol taken up by yeast can be quantitatively recovered by hydrolysis. Yeast grown in a solution containing only sugar and salts also yields inositol on hydrolysis, but in smaller amount.
L. S. Theobald.

Influence of various concentrations of phenol on the rate of alcoholic fermentation. E. Abderhalden (Fermentforsch., 1928, **9**, 389—391).—In fermentations of 2·5 g. of dextrose dissolved in 25 c.c. of phosphate buffer solution (p_H 6), using 1·0 g. of yeast, the presence of 0·1—0·2 γ of phenol generally causes a distinct acceleration of the rate of fermentation.
F. E. Day.

Liberation from yeast of substances giving the nitroprusside reaction. Y. Pourbaix and E. L. Kennaway (Biochem. J., 1928, **22**, 1112—1127).—A large number of agents have been examined for their power to liberate from yeast substances giving the nitroprusside reaction. Positive results were obtained by heating above a certain temperature, freezing, grinding, ultra-violet light, by exposure to certain saturated salt solutions or to many organic compounds of the phenol and amine classes. Many compounds inhibit the nitroprusside reaction, hence some of the negative results may be due to such suppression of the reaction. Some of the substances giving the reaction are liberated intracellularly and some extracellularly.
S. S. Zilva.

Bacterial catalase. A. Itano and S. Arakawa (Ber. Ohara Inst. landw. Forsch., 1928, **3**, 505—528).—The activity of the catalase of a thermophilic cellulose-fermenting organism is vigorous at 65° in cellulose medium, but is inhibited in dextrose broth. At 23° there is no inhibition in the latter medium, and since its hydrogen-ion concentration changes within 48 hrs. from p_H 6·75 to 4·98 at 65° but remains almost unchanged at 24°, it is concluded that the inhibition at the higher temperature is due, in part at least, to the increase in p_H. In determining the volume of oxygen liberated from hydrogen peroxide by the enzyme, the gas is collected for 10 min. from the time of starting the reaction. The potassium hydrogen phthalate of Clark's buffer solution has a marked disturbing influence on the results obtained when, in making the test, titration with permanganate of buffered solutions is substituted for the determination of the volume of oxygen liberated. Phosphate mixture has no such influence. The catalase shows greatest activity between p_H 8 and 9. At p_H less than 6·5 the activity diminishes rapidly, becoming almost nil at p_H 2·5, but it disappears more slowly on the alkaline side and is quite considerable at p_H 10. The vigour of catalase action increases with the age of the culture up to about 72 hrs., after which it decreases. The velocity of action is greatest at the end of 5 min. and diminishes thereafter. The reaction seems to be unimolecular. Activity of the catalase is at a minimum at 0° and at a maximum at 60°, but is quite considerable at 80° and is not destroyed altogether at 100°. Magnesium sulphate and copper sulphate have very slight depressive influence on the catalase action, but hydrochloric acid, mercuric chloride, and potassium cyanide have very marked effects, that of the last named being strongest.
W. McCartney.

Bacterial denitrification. M. P. Korsakova (Bull. Acad. Sci. U.S.S.R., 1927, [vi], 1221—1250).—The results of experiments with *B. fluorescens liquefaciens* and *B. pyocyaneus* show that denitrification is a process of the reduction of nitrates in anaërobic conditions, the necessary energy being supplied by the oxidation of organic matter; when the latter is not present in sufficient amount, the normal course of the reduction of nitrates is disturbed. When denitrification proceeds in presence of dextrose, the p_H of the solution does not change during the whole process, and when citric acid is supplied as organic matter, the solution becomes alkaline and the quantity of carbon dioxide developed per unit quantity of free nitrogen is double that formed in presence of dextrose. The reduction process takes place in three phases, $2HNO_3 \longrightarrow 2HNO_2+O_2$, $2HNO_2 \longrightarrow$ intermediate product$+O_2$, intermediate product $\longrightarrow N_2+H_2O+O$. The fact that this intermediate product yields one molecule of nitrogen per atom of oxygen on reduction suggests that it may be Angeli's unstable nitrosyl, HNO. The dextrose present in the solution during denitrification is oxidised completely to carbon dioxide, and the ratios of the oxidised dextrose to the reduced nitrate on the one hand and to the carbon dioxide and nitrogen formed on the other are expressed by the equations $C_6H_{12}O_6+6O_2=6CO_2+6H_2O$ and $5C_6H_{12}O_6+24KNO_3=24KHCO_3+6CO_2+12N_2+18H_2O$.
T. H. Pope.

Nitrite test as applied to bacterial cultures. G. I. Wallace and S. L. Neave (J. Bact., 1927, **14**, 377—384).—In high nitrite concentrations, favoured by peptones containing sulphur, the use of dimethyl-α-naphthylamine is preferred to that of α-naphthylamine.
Chemical Abstracts.

Composition of the active principle of tuberculin. IX. Fractional heat coagulation of the protein of tuberculin. X. Isolation in crystalline form and identification of the active principle of tuberculin. F. B. Seibert (Amer. Rev. Tuberculosis, 1928, **17**, 394—401, 402—421).—IX. Specific biological activity is associated with all the fractions obtained by coagulating the whole protein of tuberculin at different temperatures, and a protein-free active fraction could not be thus obtained. All the fractions may be derivatives of the same protein in varying stages of chemical change.

X. The specifically active substance in tuberculin is an unstable, water-soluble coagulable protein, containing no carbohydrate, and crystallisable by Hopkins' method at p_{H} 4·9. Chemical Abstracts.

Active principle of tuberculin. XI. Preparation and assay of standard undenatured tuberculin. F. B. Seibert (J. Biol. Chem., 1928, **78**, 345—362).—A solution of tuberculin, obtained by growing tubercle bacilli on a synthetic protein-free medium, may be concentrated many times with negligible loss of activity by ultra-filtration through alundum shells impregnated with a 10—12% solution of guncotton in glacial acetic acid; further removal of diffusible impurities may be effected by addition of 0·5% phenol solution to the tuberculin solution during filtration. The purified tuberculin may be assayed chemically by determining the volume of the precipitate produced by addition of trichloroacetic acid; 0·2 mg. of the purified protein is a lethal dose for a 400—500 g. tuberculous guinea-pig.

C. R. Harington.

Cultural separation of bacteria on the basis of triphenylmethane coefficients. J. W. Churchman and L. Siegel (Stain Tech., 1928, **3**, 73—80).—The crystal-violet coefficients of five Gram-positive and five Gram-negative organisms indicate that all known aërobic organisms, on the basis of their triphenylmethane coefficients, could probably be placed on a curve which would run parallel with the results of Gram staining. By making use of the differences in these coefficients cultural separations of organisms within the Gram groups may be effected.

H. W. Dudley.

Effect of chemical nature of a decoloriser on its action. I. The Gram classification. A. E. Stearn and E. W. Stearn. **II. Apparent isoelectric point.** E. W. Stearn and A. E. Stearn (Stain Tech., 1928, **3**, 81—86, 87—93).—I. Acidic decolorisers are more regular than basic substances in their action on the Gram stain.

II. The isoelectric point of a bacterial system is the hydrogen-ion concentration at which there is equal retention of anion and cation. This is determined by finding the point at which there is equal retention of acidic and basic stains when acetone is used as a decoloriser. Acidic decolorisers shift this point to a higher p_{H}, whilst basic decolorisers have the opposite effect. H. W. Dudley.

Factors influencing the staining properties of fluorescein derivatives. H. J. Conn and W. C. Holmes (Stain Tech., 1928, **3**, 94—104).—The disodium salts of eosin, erythrosin, phloxin, and rose-Bengal are indifferent stains for bacteria in dried films of soil. If, however, 0·0001—0·1% of a salt of calcium, aluminium, magnesium, or lead be added to the solutions of the dyes they stain much more intensely. Practically identical staining can be obtained by using suspensions of the calcium, aluminium, or lead salts of these dyes, although their solubilities are very small. H. W. Dudley.

New circulation hormone and its action. III. E. K. Frey and H. Kraut (Arch. exp. Path. Pharm., 1928, **133**, 1—56).—The heart stimulant previously described (A., 1926, 1168) as occurring in urine has been further purified and its physiological action on various organs has been investigated. The salts are dialysed away through parchment paper, through which the active substance passes only slowly, and concentration of the substance is then effected through adsorption on kaolin or alumina, from which it may be removed by elution with diammonium hydrogen phosphate. Precipitation with uranyl acetate in presence of alcohol is also a convenient means of purification. For further purification it may be adsorbed on finely-divided benzoic acid, which may then be removed by means of ether and alcohol. The active substance is highly unstable, being inactivated by acid or alkali or by boiling, and in its purified form is destroyed even by precipitation with alcohol. It is not yet possible to characterise the substance by chemical reactions. Its activity appears to be increased by cocaine and by calcium salts.

Blood and blood-serum contain some unknown substance capable of inactivating the active substance. Horse-serum inactivates strongly, pig-serum very little. The inactivating substance is very unstable, since, for example, blood loses its power of inactivation in a few days and also particularly rapidly when treated with acid. During inactivation by blood the substance is not destroyed but forms an inactive combination with the inactivating substance. The active substance is not choline, pituitrin, or histamine, although certain of its physiological effects are similar to those of the last-named substance. The compound appears to be present normally in the blood, but usually in the form of its inactive combination and only exceptionally in the free condition. It is considered to be a hormone and its physiological effects are in general such as facilitate muscular activity. W. O. Kermack.

Influence of adrenaline on the protein metabolism of isolated organs. B. S. Sentjurin (Arch. exp. Path. Pharm., 1928, **133**, 233—241).—The influence of adrenaline and, in the first place also, of Ringer–Locke solution on the secretion of proteins by isolated organs has been examined. Determinations of total nitrogen and of residual nitrogen were made and the amount of protein nitrogen was obtained by difference. Prolonged action of Ringer–Locke solution produces gradual but continuous decrease in the amount of residual nitrogen and an initial decrease followed by increase in that of protein nitrogen. Ordinarily the absolute amount of protein nitrogen is greater than that of residual nitrogen and the difference increases continuously in course of time. Adrenaline causes the amount of residual nitrogen to increase, but its effect on protein nitrogen is variable. The ratio of residual nitrogen to protein nitrogen increases. Although the experiments were made for the most part on testicles, the behaviour of other organs is the same. W. McCartney.

Action of adrenaline on the mobilisation of sugar in muscle. W. Grunke and A. Kairies (Arch. exp. Path. Pharm., 1928, **133**, 63—68).—Per-

fusion of the muscle of the frog with Ringer's solution containing adrenaline causes the removal of a greater quantity of sugar than when adrenaline is absent, although the effect of adrenaline on the muscle is less marked than on liver when similarly perfused.
W. O. Kermack.

Effect of insulin on protein metabolism. V. C. Kiech and J. M. Luck (J. Biol. Chem., 1928, 78, 257—264).—Administration of insulin to normal rats caused an increase in the carbamide content and a decrease in the amino-acid nitrogen content of the whole animal, indicating an increase in the rate of catabolism of amino-acids together with a decrease in the rate of formation of the latter by degradation of protein.
C. R. Harington.

Effect of insulin on sugar content of erythrocytes. H. C. Trimble and S. J. Maddock (J. Biol. Chem., 1928, 78, 323—336).—The sugar content of erythrocytes is better determined by direct analysis of the separated cells than indirectly by determination of the sugar content of whole blood and plasma and calculation from the cell-volume. Administration of insulin to diabetic patients and to depancreatised dogs causes an almost parallel decrease of sugar in red blood-corpuscles and plasma, no signs of a sudden preliminary drop in the former being observed.
C. R. Harington.

Effect of insulin on the metabolism of striped muscle. K. Kimura and H. Takahashi (Tôhoku J. Exp. Med., 1928, 10, 215—247).—Injection of insulin lowers the oxygen consumption of the dog's gastrocnemius and diminishes the sugar content of the blood circulating through the muscle through the arrest of cell activity. Insulin increases the hæmoglobin content of the blood, and diminishes the serum-globulin. The changes in serum sodium chloride are irregular.
Chemical Abstracts.

Insulin hypoglycæmia and insulin shock in man. O. Klein and H. Holzer (Z. klin. Med., 1928, 107, 94—112; Chem. Zentr., 1928, i, 1200).—An examination of the relation between insulin (hypoglycæmic) shock, the reserve carbohydrate, the formation of carbohydrate, and the alkali reserve.
A. A. Eldridge.

Insulin, folliculin, and glycæmia in normal dogs. F. Rathery, R. Kourilsky, and (Mlle.) Y. Laurent (Compt. rend., 1928, 187, 255—257).—Folliculin and insulin exert opposing influences on glycæmia in dogs. In the simultaneous injection of folliculin (10 units) and insulin (20 units) into animals of either sex, folliculin prevents insulin from exerting its normal effect on the initial hyperglycæmia produced by the ingestion of dextrose, and retards the later hypoglycæmia due to insulin. In starving animals the hypoglycæmic effect of insulin is decreased.
R. Brightman.

Hormones and vitamins. New definitions of vitamins. L. Randoin and H. Simonnet (Bull. Soc. Chim. biol., 1928, 10, 745—756).—Vitamins may be considered to be hormones which are produced from sources other than the organism on which they eventually exert their influence (exohormones as distinct from endohormones, formed by internal secretion).
G. A. C. Gough.

Assay of vitamin-*A*. K. H. Coward and K. M. Key (Biochem. J., 1928, 22, 1019—1025).—Tests are described in which subnormal growth of rats on a deficient diet graded quantitatively to the dose has been obtained without being followed by premature slackening. Rats apparently in a similar physiological or pathological condition may react by resumption of rapid growth, by immediate resumption of subnormal growth, or by a long latent period followed by a resumption of normal growth, on the same dose.
S. S. Zilva.

Absorption spectrum of vitamin-*A*. R. A. Morton and I. M. Heilbron (Biochem. J., 1928, 22, 987—996).—From spectroscopic examination of various oils and preparations it is concluded that the presence of vitamin-*A* is characterised by an absorption band with a maximum at 328 μμ. Sometimes, as in the case of dog-fish oil, this characteristic band may be masked by superimposition of a neighbouring band. The destruction of the vitamin-*A* of an oil is accompanied by the disappearance of the band at 328 μμ. It is probable that one of the decomposition products of vitamin-*A* has an absorption band near 275—285 μμ.
S. S. Zilva.

Colour tests for sterols and for vitamin-*A*. II. Spectroscopic study of the colorations attributed to vitamin-*A*. F. Wokes (Biochem. J., 1928, 22, 997—1006).—From the spectroscopic studies of the colours produced by arsenic or antimony trichlorides on a number of cod-liver oils and concentrates, the vitamin-*A* potency of which has previously been assessed biologically, it has been ascertained that in the case of the former reagents bands at about 587 and 475 μμ were discernible, whilst antimony trichloride gave bands at about 614 and 530 μμ. There is a gradual loss in the blue and a gain in the red colour when the chromogen remains in contact with either reagent. This is accompanied spectroscopically by a gradual transition from the stage giving the "initial" band (at about 587 or 615 μμ) to the stage giving the "second" band (at about 475 or 530 μμ).
S. S. Zilva.

Vitamin-*A* formation. The feeding of etiolated wheat shoots to rats kept in darkness. T. Moore (Biochem. J., 1928, 22, 1097—1101).—These shoots were found to be an effective source of vitamin-*A* when tested on rats under conditions involving the use of the minimum of red light illumination.
S. S. Zilva.

Relative stability of vitamin-*A* from plant sources. H. C. Sherman, E. J. Quinn, P. L. Day, and E. H. Miller (J. Biol. Chem., 1928, 78, 293—298).—Heating of tomato juice at 95—99° for 4 hrs. in presence or absence of oxygen destroyed about 17% of the vitamin-*A*; the rate of destruction of the vitamin during anaërobic heating was not affected by altering the p_H of the juice from its natural value (4·2) to 9·2. Anaërobic heating of an olive oil extract of dried spinach caused 20% destruction of vitamin-*A*, whilst similar treatment of a solution of butter in olive oil destroyed 33% of the vitamin.
C. R. Harington.

Tripartite nature of vitamin-*B*. R. R. Williams and R. E. Waterman (J. Biol. Chem., 1928, 78, 311—322).—Pigeons were kept on a synthetic diet in which vitamin-B_1 was supplied in the form of a fuller's earth adsorbate of a dialysed yeast extract, and -B_2 as autoclaved yeast. Such birds showed a marked improvement on the addition of air-dried brewer's yeast to the diet. The factor thus supplied could not be any known vitamin, and is thought to be a third, heat-labile component of vitamin-*B*.

C. R. Harington.

Multiple nature of vitamin-*B*. A. G. Hogan and J. E. Hunter (J. Biol. Chem., 1928, 78, 433—444).—Irradiation with ultra-violet light destroys the growth-promoting properties of yeast and of vitamin-*B* preparations derived therefrom, while leaving the antineuritic properties unimpaired.

C. R. Harington.

Glutathione and reducing power of muscle in vitamin-*B* deficiency. H. Yaoi (Proc. Imp. Acad. Tokyo, 1928, 4, 233—235).—The muscle of pigeons fed on a diet deficient in vitamin-*B* has a weaker reducing action on methylene-blue than normal pigeon muscle. No material difference is detectable in the glutathione content in the two cases.

J. H. Birkinshaw.

Comparative variations in the content of water, fatty acids, and cholesterol in the liver and spleen of guinea-pigs on a normal diet and on one deprived of antiscorbutic vitamin. (Mlle.) L. Randoin and (Mlle.) A. Michaux (Compt. rend., 1928, 187, 146—149).—The fresh liver of normal guinea-pigs contains 0·21% of cholesterol, 1·81—2·26% of fatty acids, and 72·5—74·6% of water. When fed on diets deficient in vitamin-*C*, the fatty acids increase gradually to 3·0% in the final stages, the cholesterol tending to increase slightly but within the limits of variations with individual animals. The lipocytic coefficient (ratio of cholesterol to fatty acids) thus decreases with the progress of scorbutic symptoms. The weight of the spleen is very variable, but on an average the normal spleen contains 78·3% of water, 0·4% of cholesterol, and 1·4% of fatty acids. In acute scurvy the spleen increases in volume and weight after some time. In the final stages the cholesterol decreases sharply, the fatty acids to a slight extent, and the water content tends to increase. In all these variations the lipocytic coefficient is lower than in the case of animals fed on a complete artificial diet (cf. A., 1926, 1181; 1927, 282).

R. Brightman.

Biological assay of cod-liver oil. G. Adams and E. V. McCollum (J. Biol. Chem., 1928, 78, 495—524).—No biological method has been devised for the evaluation of the absolute antirachitic potency of cod-liver oil. For the comparison of different samples of oil determination of the ash content of the bones of the experimental animals is of little value. Of greater utility is the determination of the product of the ionic concentrations of calcium and phosphorus in the blood; the results of such determinations can be correlated with those obtained by histological observations. The conclusion of Holt (A., 1925, i, 1209), that the value of the above-mentioned ionic product is less than 8×10^{-25} in active rickets, is confirmed.

C. R. Harington.

Examination of irradiated zymosterol for the presence of vitamin-*D*. E. M. Hume, H. H. Smith, and I. Smedley-MacLean (Biochem. J., 1928, 22, 980—986; cf. Smedley-MacLean, this vol., 329).—Zymosterol is not capable of being activated by ultra-violet irradiation. This was ascertained by biological tests in which four different diets were employed, namely, a diet deficient in both fat-soluble vitamins, the same containing wheat germ (this vol., 556), McCollum's diet 3143, and Sherman and Pappenheimer's diet. Comparisons have also been obtained for the minimum doses of irradiated ergosterol necessary to produce an effect when the different diets are employed.

S. S. Zilva.

Variations in the process of photosynthesis. N. A. Maximov and T. A. Krassnosselski-Maximov (Ber. deut. bot. Ges., 1928, 46, 383—391).—The process of photosynthesis does not take place at a uniform rate, but varies widely in its intensity within periods of a few minutes. When measured over longer periods the total amount of carbon dioxide involved in the process shows a fair regularity. A possible connexion is suggested between this phenomenon, the rhythmic motion of the stoma, and the periodicity of transpiration.

A. G. Pollard.

Application of the Donnan equilibrium to the ionic relations of plant tissues. G. E. Briggs and A. H. K. Petrie (Biochem. J., 1928, 22, 1071—1082).—The conception of a simple Donnan membrane equilibrium operating between two homogeneous phases is inadequate to explain the phenomena of ionic intake by plants.

S. S. Zilva.

Cell phosphatides of plants. II. B. H. Cranner (Meld. Norges Landbruks, 1927, 7, 611—643).—A study of the reactions of phosphatide extracts with solutions of acid and alkaline dyes.

Chemical Abstracts.

Water content of leaves in relation to the wilting of plants. R. Kôketsu (Proc. Imp. Acad. Tokyo, 1928, 4, 229—230).—The ratio between the water content at the time of critical wilting and that at full turgidity is probably specific for a given plant when cultivated in a given soil.

J. H. Birkinshaw.

Chemical composition of vegetable seed fats in relation to the natural order of plants. T. P. Hilditch (Proc. Roy. Soc., 1928, B, 103, 111—117).—The existing data on the chemical nature of various seed fats are discussed with reference to botanical order. It is shown that, although other acids always exist in fair to considerable proportions, the four acids lauric, myristic, erucic, and petroselic are specific in the respective cases of the four orders, *Palmæ*, *Myristiceæ*, *Cruciferæ*, and *Umbelliferæ*.

E. A. Lunt.

Potassium and sodium in sea-weeds. G. Bertrand and M. Rosenblatt (Compt. rend., 1928, 187, 266—270).—Immersion of sea-weeds in distilled water results first in a decrease and then in an increase of the sodium : potassium ratio in some cases but has little effect in others. All the species examined contained potassium. For plants washed twice in water the ratio (Na : K) varies from 1 : 4·20 to 1 : 0·58.

G. A. C. Gough.

Occurrence of manganese in trees. M. KLEINSTUCK (Chem.-Ztg., 1928, 52, 598—599).—The manganese content of different parts of various trees growing in the valley of the Elbe is recorded. The bark and leaves have in general a higher manganese content than the wood, and the manganese content of the leaves increases rapidly during the season. It is suggested that the manganese acts as a catalyst in the organs of assimilation and that its catalytic activity is destroyed by sulphur dioxide; this would explain the serious effect of sulphur dioxide on vegetation. A. R. POWELL.

Manganese in plants: its importance in plant metabolism. W. B. S. BISHOP (Austral. J. Exp. Biol. Med. Sci., 1928, 5, 125—141).—Manganese is present in many varieties of seeds, plants, and fruits; it is not evenly distributed throughout the plant and is at its highest concentration in those parts where there is most intense chemical activity. Manganese is essential for plant development. Experiments were made with plants grown in neutral and in acid media, with the addition of manganese sulphate in amounts similar to those present in a water-soluble condition in average soil, as well as in much larger amount. Results showed that within rather narrowly-defined limits manganese has beneficial effects on plant growth and that calcium reduces the toxicity of high concentrations of the element. The effect of manganese is not due to reduced absorption of iron by the plant, but there is some relation between the presence of manganese and carbon assimilation. The determinations of manganese were made colorimetrically by the persulphate method. W. MCCARTNEY.

Determination of the salt content from the $p_{\rm H}$ value of apple juice. Mineral content of the juice and whole apple. D. HAYNES and J. W. BROWN (Biochem. J., 1928, 22, 947—963).—It is possible to obtain an assessment of the salt content of the apple as "equivalent potash" by comparing the $p_{\rm H}$ and titratable acidity of the juice with the acidity and $p_{\rm H}$ of mixtures of malic acid and potassium malate of known concentration. Acidity titrations, $p_{\rm H}$, and "equivalent potash" are given for samples of Lane's Prince Albert and Cox's Orange Pippin picked at the normal season and also earlier and later. Similar measurements on samples from a single picking of other kinds of apple are also given. The same percentage of potash was found in the expressed juice as in the whole apple. Larger percentages of magnesia and lime, some of which was most probably of cell-wall origin, were found in the juice than in the whole apple. There is some evidence that this dissolution of cell-wall material by the juice varies with the acidity of the juice. S. S. ZILVA.

Chemical composition of juices of American apples. J. S. CALDWELL (J. Agric. Res., 1928, 36, 407—417).—Data extending over a period of 3 years relating to the total sugar, astringency, and acid content of the juice of 98 varieties of apple are in agreement with the previous conclusions of the authors that climatic conditions during the period of development and maturity of the fruit produce consistent effects on its chemical composition, the character of these effects being similar in large groups of trees of dissimilar origin. E. A. LUNT.

Composition of American-grown French cider apples and other apples of like character. J. S. CALDWELL (J. Agric. Res., 1928, 36, 391—406).—Data are given for the total astringency, sugar, and acid values of the juice of 82 varieties of apple of French, American, and Siberian origin, with a view to the preparation of a non-fermented beverage juice. The results indicate that the composition of the French cider apples remains unaltered after 23 years' growth in America either at an elevation of 2170 ft. or at sea-level. E. A. LUNT.

Changes produced in apples by the use of cleaning and oil-coating processes. J. R. WELLER (J. Agric. Res., 1928, 36, 429—436).—The application of a coating of paraffin to apples causes a reduction in the respiratory rate of the fruit even after 8 months of cold storage, and the oiled fruit subsequently loses weight and shrinks less rapidly at market temperature than the unoiled fruit. The dessert quality of the fruit is unaffected. E. A. LUNT.

Nitrogen metabolism of *Pyrus malus*, L. I. Influence of temperature of desiccation on water-soluble nitrogenous constituents and separation of water-soluble protein from non-protein constituents. II. Distribution of nitrogen in the insoluble cytoplasmic proteins. W. THOMAS (Plant Physiol., 1927, 2, 55—66, 67—70).—In respect of coagulation and proteolysis, the optimal temperature for desiccation is 60°. Direct extraction with water produces less disturbance in the protein and non-protein fractions due to *post mortem* changes than methods employing cytolytic agents. The proteins are best separated by means of colloidal ferric hydroxide. Little qualitative change in the nature of the insoluble leaf proteins occurs during development; the presence of a single protein is assumed. The carbohydrate–nitrogen relations of plants are discussed. CHEMICAL ABSTRACTS.

Development of the wheat kernel. C. E. SAUNDERS (Sci. Agric., 1928, 8, 524—531).—The rate of deposition of protein is greatest when the kernel is gaining in weight most rapidly. During the first few days of the experiment the deposition of non-protein material was more rapid than that of protein. CHEMICAL ABSTRACTS.

Quantitative variations of enzymes in grains of wheat in the course of ripening, resting, and germinating. A. N. BACH, A. I. OPARIN, and R. A. VENER (Trans. Karpov Inst. Chem., 1926, No. 5, 62—70).—During ripening, two opposing processes occur simultaneously: formation of active enzymes and their transition into inactive zymogens; the latter become transformed into enzymes in the course of germinating. Catalase and peroxidase decrease little, whilst amylase and protease disappear, during ripening; all increase largely during germination. CHEMICAL ABSTRACTS.

Development of cotton bolls and the rate of formation of gossypol in the cotton seed. W. D. GALLUP (J. Agric. Res., 1928, 36, 471—480).—The chemical composition of cotton bolls with reference to ash, nitrogen, carbohydrate, ether-soluble material, and fibre content has been determined as a function of the age of the boll. The development of oil and gossypol occurs simultaneously in the cotton seed during a short and well-defined period between the 24th and 32nd days of growth. E. A. LUNT.

Transport of carbohydrates in the cotton plant. II. Factors determining the rate and direction of movement of sugars. T. G. MASON and E. J. MASKELL (Ann. Bot., 1928, **42**, 571—636).—The movement of sugar from leaf to root in the cotton plant was examined by regional analysis of the plant-tissue and shown to follow a definite concentration gradient. This occurred when the normal direction of sugar movement was artificially reversed, although the change in concentration gradient lagged behind the directional change. The amount of sugar passing down the stem was decreased by the removal of portions of bark, but the sugar passing unit sectional area of the restricted channel increased proportionally with the increased concentration gradient. Within the bark the concentration of sucrose increases from outside to inside, and that of reducing sugars in the opposite direction. The radial concentration gradient of sucrose varied considerably, but that of reducing sugars was fairly stable. In a given area of bark there is a high positive correlation between the percentage of sieve tubes and the sucrose concentration and a correspondingly high negative correlation for reducing sugars. Generally speaking, longitudinal transport of sugars takes place through the sieve tubes at rates varying with the concentration gradient and the process is akin to, but far more rapid than, simple diffusion. Lateral movement of sugar, *e.g.*, from bark to wood, is similar in nature and rate to physical diffusion. A. G. POLLARD.

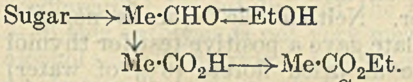
Phosphorus compounds in plants. I. Exosmosis of phosphorus compounds from plants. W. ZALESKI and W. MORDKIN (Biochem. Z., 1928, **195**, 415—420).—The functional permeability of different organs of the plant is different and changes during the various stages of growth. Resting seeds permit of the diffusion of a greater amount of organic phosphorus compounds than germinating and unripe seeds. The amount of phosphatide passing into water can scarcely be regarded as arising merely from the limiting surface of the cells. P. W. CLUTTERBUCK.

Influence of sodium carbonate and calcium chloride on the acidity of the sap of the maize plant. II. S. KARASIEWICZ (Bull. Soc. Chim. biol., 1928, **10**, 702—713; cf. A., 1927, 798, 908).—The predominant effect of media containing calcium chloride on the total acidity of the plant, as distinct from the effect of sodium carbonate, is largely due to the fact that the soluble sodium salts are easily excreted by the roots. Water containing even small amounts of the two salts (0·2% of calcium chloride and 0·01% of sodium carbonate) increases the growth. G. A. C. GOUGH.

Action of mixed reagents on the viscosity of protoplasm. H. TIMMEL (Protoplasma, 1927, **3**, 197—212; Chem. Zentr., 1928, i, 1049—1050).—Centrifuge experiments were carried out with the chloroplast of various plants and single or mixed salts, particularly potassium, and organic compounds. A. A. ELDRIDGE.

Liberation of the free iodine of *Laminaria flexicaulis*. P. DANGEARD (Compt. rend., 1928, **186**, 1371—1373).—Slow liberation of iodine from the thallus of *L. flexicaulis* takes place continuously in all except very young plants. The output of iodine is increased temporarily by damaging the tissue either by incisions or by acids. There is evidence that the iodine cells lie near the surface of the thallus. E. A. LUNT.

Mechanism of fruit-ester formation by *Willia anomala*. M. YAMADA (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 73—76).—The following mechanism for the production of ethyl acetate is proposed :—



$$\begin{array}{l}\text{Sugar}\longrightarrow\text{Me}\cdot\text{CHO}\rightleftharpoons\text{EtOH}\\ \qquad\qquad\downarrow\\ \qquad\qquad\text{Me}\cdot\text{CO}_2\text{H}\longrightarrow\text{Me}\cdot\text{CO}_2\text{Et}.\end{array}$$

CHEMICAL ABSTRACTS.

Formation of starch in the haricot. H. COLIN and R. FRANQUET (Compt. rend., 1928, **187**, 309—311).—Little starch is found in the stalks, stems, roots, leaves, or the young seeds of haricot; the ripened seeds contain 35·66%, which almost completely disappears on germination. G. A. C. GOUGH.

Theory of starch formation. K. JOSEPHSON (Z. physiol. Chem., 1928, **174**, 179—190).—It is assumed that there is a single parent substance (an anhydroglucose) which gives rise to the different constituents of starch (amylose and amylopectin). Two molecules of anhydroglucose unite to give a disaccharide anhydride which contains both α- and β-glucoside linkings. The union of the 2 mols. of anhydroglucose is complete in the amylose fraction, but not in the amylopectin fraction; when native starch is converted into the so-called soluble starch of Zulkowsky, the reaction in the amylopectin fraction is completed. Amylopectin consists of the anhydroglucose or the disaccharide anhydride combined with some other grouping, perhaps a hexosephosphate or similar compound. A. WORMALL.

Composition of aquatic plants of Lake Mendota. II. *Vallisneria* and *Potamogeton*. H. A. SCHUETTE and H. ALDER (Trans. Wis. Acad. Sci., 1928, 23, 249—254). CHEMICAL ABSTRACTS.

Influence of geographical factors on the chemical composition of plants. N. N. IVANOV (Ann. State Inst. Exp. Agron. [Russia], 1926, **4**, 23—32).—The protein content of wheat grown at the same longitude is greater for more southerly latitudes (46° 25′, 55° 48′); at the same latitude it is greater for a more easterly longitude (30° 38′, 100° 22′). The water régime influences the protein content of wheat. Similar results were obtained with barley, oats, and rye. CHEMICAL ABSTRACTS.

Spectrum and pharmacology of chlorophyll. F. GRILL (J. Amer. Pharm. Assoc., 1928, **17**, 422—427).—The spectrum of chlorophyll dissolved in different solvents is described. Heat seems to have no appreciable effect on the spectrum, but the intensity is reduced with age. Chlorophyll extracts, but not the chlorophyll granules themselves, have a general stimulating action on all the tissues and organs of animals. Earthworms are very susceptible to the action of chlorophyll extract, and their use is suggested for the biological examination of commercial preparations. E. H. Sharples.

Digitalic acid. P. Bourcet and A. Fourton (Compt. rend., 1928, **186**, 1577—1578).—The impure digitalic acid described by Kolipinski (Interstate Med. J., 1913, **20**, 1117) as being without physiological activity is impure succinic acid. The unstable, active acids are found in larger amounts in the fresh plant. G. A. C. Gough.

Corolla of *Monarda punctata*, L. H. G. Hewitt (J. Amer. Pharm. Assoc., 1928, **17**, 457—458).—The florets on distillation with xylene gave 68—70% of water. Neither the aqueous nor the hydrocarbon distillate gave a positive test for thymol or carvacrol. The air-dried florets (6% of water) contained 10·49—10·92% of ash (insoluble 5·52—6·11%) and on steam distillation gave 3·45% of oil (d^{22} 0·9652) containing little, if any, thymoquinol. E. H. Sharples.

Principles of two types of *Combretum* seeds. V. Hasenfratz and R. Sutra (Compt. rend., 1928, **186**, 1860—1862).—The pulverised seeds of *C. Bernierianum* when extracted with carbon disulphide yielded 10% of a light yellow oil, consisting chiefly of palmitin and olein with a small quantity of other glycerides. The seeds also contained sucrose. *C. subumbellatum* yielded the same products. No trace of a glucoside was found. J. D. Fulton.

Mannan of iris seed. H. Colin and A. Augem (Bull. Soc. Chim. biol., 1928, **10**, 822—825).—The mannan of iris seed yields mannose (82%) and arabinose (18%) on hydrolysis with boiling 3% sulphuric acid. The sugar reserve of the seed is present probably as a mannoaraban. Sucrose, but no free mannose is found in the young seeds. G. A. C. Gough.

Enzymic hydrolysis of melezitose and turanose. T. Aagaard (Tidsskr. Kjem. Bergv., 1928, **8**, 5—9, 16—20, 35—39).—Bourquelot's method has been utilised in an attempt to determine the constitution of the above sugars. Melezitose was prepared by Tanret's method from Abyssinian manna. The pure product had m. p. 152°, and had a rotation $[\alpha]_D$ +88·4°. Turanose could not be satisfactorily prepared from this by Tanret's method (cf. A., 1906, i, 560), but was finally obtained by carefully heating a 10% solution of melezitose on the water-bath for 45 min. with 1% sulphuric acid. The dextrose simultaneously produced was removed by subsequent fermentation, which does not affect the turanose. The product had $[\alpha]_D$ +73°, and a reducing power of 0·566 referred to dextrose as unity. A 1% solution of turanose alcoholate, $C_{12}H_{22}O_{11},0{\cdot}5EtOH$, treated with brewer's yeast and kept at 30°, was rapidly hydrolysed, the decomposition into dextrose and lævulose being practically complete after 2 hrs. Similar experiments with emulsin, rhamnodiastase, and autolysed yeast containing invertase had no effect. The hydrolysis in the first case is ascribed to the α-glucosidase present in the yeast, this view being confirmed by an experiment using yeast which had been precipitated and washed with alcohol, and dried in a vacuum. This treatment destroys α-glucosidase, and the resulting product had no action on turanose. Turanose is consequently to be regarded as an α-glucoside of lævulose, just as maltose can be regarded as an α-glucoside of dextrose. Melezitose is regarded as having the composition

$$\overbrace{\text{dextrose}<\text{lævulose}}^{\text{turanose}}\underbrace{<>\text{dextrose}}_{\text{sucrose}};$$

this view is supported by the fact that the disaccharide turanose formed from it on hydrolysis does not reduce a hypoiodite solution, and must consequently be regarded as having a ketonic structure. *Aspergillus niger* partly hydrolyses melezitose into turanose and dextrose, but owing to the presence of other enzymes in the extract, secondary reactions take place, a part of the turanose being decomposed, so that no definite conclusions can be reached from the results. The presence of a specific enzyme "melezitase" in the extract is suggested. Melezitose is not acted on by invertase; with methylemulsin a slow decomposition takes place. α-Glucosidase yields lævulose and dextrose, but the results throw no light on the composition of the original sugar. The above experiments do not support the view of Kuhn and van Grundherr (cf. A., 1926, 1127) that there is a "glucoinvertase" present in the extract of *A. niger* which causes the hydrolysis of melezitose, and that ordinary invertase is a fructoinvertase.

A series of tables showing the effect of various enzymes on sugars of known composition is also given. H. F. Harwood.

Carotin; a pigment of honey. H. A. Schuette and P. A. Bott (J. Amer. Chem. Soc., 1928, **50**, 1998—2000).—Carotin (0·01%) was separated from a highly pigmented honey by the method of Palmer and Eckles (A., 1914, i, 624). H. E. F. Notton.

Chemical constitution of chondriosomes and protoplasts of plants. P. Milovidov (Compt. rend., 1928, **187**, 140—142).—The mycelium of *Saprolegnia* gives positive tests with the following reagents: Derrien and Furchini's, Zacharias', Millon's, xanthoprotein, quinol, phosphomolybdic acid, biuret, eosin, and iodine–iodide. The spherical protoplasts of the epidermis of *Tradescantia* and the shoots of *Elodea canadensis* give positive results with the same reagents (only feebly with eosin), and the protein reactions thus appear to be the same for the chondriosomes of these different types of plant. It is concluded that there is no essential chemical difference between animal and plant chondriosomes. R. Brightman.

Protein content of grass, chiefly meadow foxtail (*Alopecurus pratensis*), as influenced by frequency of cutting. F. T. Shutt, S. N. Hamilton, and H. H. Selwyn (J. Agric. Sci., 1928, **18**, 411—420).—From analyses of the produce of plots cut at frequent intervals and those cut for hay, it is concluded that in a season's growth a larger amount of digestible protein was produced on the plot cut every third week than on the plot cut as hay. H. J. G. Hines.

Does the pea plant fix atmospheric nitrogen? D. Burk (Plant Physiol., 1927, 2, 83—90).—When grown in culture solutions under sterile conditions, *Pisum sativum* (dwarf variety) showed, statistically, a loss of nitrogen large enough to hide evidence of fixation. Chemical Abstracts.

Tabacin, the toxic principle of tobacco. N. A. Barbieri (Atti R. Accad. Lincei, 1928, [vi], 7, 764—768).—Treatment of unfermented Kentucky tobacco, dried either by direct heat or in the sun, with a series of organic and aqueous solvents yields nine distinct fractions, comprising xanthophyll, chlorophyll, cellulose, fats, etc., together with *tabacin*, which is a yellow, waxy, hygroscopic substance of irritating, caustic taste and acid reaction, and with an odour resembling that of methylamine. Tabacin, which is composed of a glucoside with a nitrogen-containing acid, emits irritant vapours of tabacol at about 110°, and is rapidly transformed into its components, tabacol, tabacinic acid (non-toxic), and a sugar, by cold 2% potassium hydroxide solution. Tabacol, like tabacin, loses ammonia and yields nicotine on protracted heating with concentrated potassium hydroxide; it has an irritating acrid odour. Both tabacin and nicotine, whether obtained commercially or prepared from tabacol, are fatal to guinea-pigs in doses of 9 mg. per 100 g. of body-weight. Tabacol is a very powerful, convulsant poison, with an effect, when injected, resembling those of hydrocyanic acid and strychnine together. Scafatin, the yellow colouring matter of tobacco, is neutral and is insoluble in all known neutral solvents except water.

T. H. Pope.

Constituents of *Typha angustata*, Bory. et Chaub. M. Fukuda (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 711—717).—See this vol., 560.

Glutelins. IV. Glutelins of maize (*Zea mays*). D. B. Jones and F. A. Csonka (J. Biol. Chem., 1928, 78, 289—292).—Maize meal was extracted with 60% alcohol containing sodium hydroxide, and the crude glutelin obtained by acidification of the extract; dissolution of the precipitate in aqueous sodium hydroxide and treatment with ammonium sulphate to 3% saturation gave a precipitate of α-glutelin, figures for the nitrogen distribution of which are given; treatment of the mother-liquor with ammonium sulphate to 16% saturation gave a small amount of β-glutelin. C. R. Harington.

Metabolism of *Aspergillus oryzæ*. II. H. Tamiya (Acta Phytochim., 1928, 4, 77—213; cf. A., 1927, 906).—The effect of various metallic ions on the growth and metabolism of *A. oryzæ* in media of different p_H has been examined. The p_H–growth curves show no marked alteration from the normal when salts of the alkali metals are added, whereas calcium, strontium, and barium ions increase growth at lower p_H values and have a retarding action in more alkaline solutions. Aluminium, iron, cobalt, and nickel ions have an action similar to that of the alkaline-earths, whereas small amounts of zinc, copper, mercury, and silver ions promote growth at about p_H 4—5 and inhibit at higher or lower p_H. Double-peaked growth–p_H curves, similar to the normal curve and having a middle minimum at p_H 5—6, are obtained with the usual culture method (spore cultures), when these salts, except those of copper, mercury, silver, and zinc, are added. These characteristic curves are due to the young mycelia and no double-peaked curves are obtained with well-grown surface cultures, which are also more resistant than spore cultures to alkalis. Growth stimulated by the salts of heavy metals, and to a smaller extent that promoted by the salts of the alkaline-earth metals, is often accompanied by a diminished kojic acid production, whilst a deficiency of nitrogen in the medium favours the formation of this acid. In the absence of oxygen the conidia do not germinate, and instead of growth of the fungus an alcoholic fermentation occurs, this fermentation being greatest with young mycelia and at p_H 5—6; the fermentation is accompanied by autolysis of the fungus, but at p_H 5—6 this autolysis is not very marked and the ratio alcohol : carbon dioxide is approximately 1. Aërobic respiration is more marked in earlier stages of the development of the fungus and has an optimum reaction of p_H 6—7. Deprivation of nutrient salts leads to a diminution of growth under aërobic conditions, but has no marked effect on anaërobic culture. Growth under aërobic conditions is promoted by oxalic acid, zinc sulphate, and lactic acid, the effect decreasing in this order, whilst ferrous chloride and calcium carbonate have an inhibitory influence; anaërobically, calcium carbonate only has any influence, and the inhibition observed with this salt is attributed to its alkalinity.

The relationship between aërobic and anaërobic respiration has been studied. Admission of oxygen after a period of anaërobiosis results in normal growth and respiration, and anaërobiosis exerts no influence on the subsequent aërobiosis. The ratio of anaërobically produced alcohol to aërobically produced carbon dioxide is somewhat smaller than that found by various authors for other plants, and the value decreases with the ageing of the culture; if corrections are made for the increase in weight of the fungus during aërobiosis, however, the ratio is approximately 1/6 and is independent of the age of the culture. The energy production in anaërobiosis is therefore about 1/50 of that in aërobiosis. With surface cultures, nitrates are better sources of nitrogen than ammonium salts at lower p_H values, but the converse is found for p_H 7—8. A. Wormall.

Cytochrome in fungi. H. Tamiya (Acta Phytochim., 1928, 4, 215—218).—Cytochrome has been detected spectroscopically in surface cultures of *Aspergillus oryzæ*. Older cultures give the characteristic absorption bands to a smaller extent or not at all, and there is a parallelism between cytochrome content and intensity of respiration. Anaërobiosis leads to a disappearance of the cytochrome, which reappears, however, when aërobiosis follows. Mycelia cultivated anaërobically by shake culture or anaërobic surface cultures of the fungus, which give therefore no cytochrome bands, yield more marked hæmochromogen–pyridine reactions than do aërobic cultures. A. Wormall.

Stimulating effect [of sugars] on the invertase of *Penicillium glaucum*. Z. I. Kertész (Fermentforsch., 1928, **9**, 300—305).—*Penicillium glaucum*, grown in a medium containing mineral salts and glycerol, produced invertase only when sucrose or raffinose was also present. Invert-sugar and lactose caused no invertase formation. With sucrose, the optimum concentration for invertase production was about 30—40%. F. E. Day.

Mechanism of degradation of fatty acids by mould fungi. II. P. D. Coppock, V. Subramaniam, and T. K. Walker (J.C.S., 1928, 1422—1427).—In continuation of previous work (this vol., 804) the action of *Aspergillus niger* on calcium *n*-butyrate, *n*-valerate, and *iso*valerate has been investigated. With calcium butyrate, butyric acid, β-hydroxybutyric acid, acetoacetic acid, and acetone are successively produced. No formation of crotonic acid could be detected. With the *n*-valerate, β-hydroxyvaleric acid and methyl ethyl ketone are produced. With the *iso*valerate β-oxidation again occurs, first yielding β-hydroxy*iso*valeric acid, which is then degraded to acetoacetic acid and finally acetone, this result being in agreement with the observed physiological degradation of this acid (cf. Dakin, " Oxidation and Degradation in the Animal Body," 1922) and contrary to Meyer's results obtained by permanganate oxidation *in vitro* (A., 1883, 983). The authors thus differ from Stokoe (this vol., 335) and Derx (A., 1924, i, 1119), who presume that a β-keto-acid is the first product of oxidation of a straight-chain acid. J. W. Baker.

Grey speck disease of oats. G. Samuel and G. S. Piper (J. Agric. S. Australia, 1928, **31**, 696—705, 789—799).—A disease of oats grown on certain alkaline soils, and identified as grey speck disease (Dörrfleckenkrankheit), is shown to be due to manganese deficiency in the plant and may be cured by treatment of the soil with manganese sulphate. Soil sterilisation by heat, which increased the solubility of manganese, completely prevents, addition of ammonium sulphate or chloride partly cures, whilst addition of lime increases, the disease. E. A. Lunt.

Determination of the reaction of swamp waters. I. A. Smorodincev and A. N. Adova (Bull. Soc. Chim. biol., 1928, **10**, 806—811).—The values obtained by the use of hydrogen and quinhydrone electrodes in the absence of buffer solutions often show wide variations (up to 0·597 p_H). Colorimetric determinations using buffer solutions and nitrophenol indicators are satisfactory and permit distinction between waters from *Sphagnum* (p_H 3·82—5·6) and those from *Carex* (p_H 7·4—8·47). G. A. C. Gough.

Colorimetric determination of lactic acid. A. Hansen, O. Riesser, and T. Nagaya (Biochem. Z., 1928, **196**, 301—308).—The colorimetric method of Mendel and Goldscheider (A., 1926, 212) is successfully applied to the determination of lactic acid in muscle, brain, and other physiological substances. P. W. Clutterbuck.

Absorption paper used in the micro-analytical methods of Bang. F. Nepveux and A. Thépénier (Bull. Soc. Chim. biol., 1928, **10**, 699—701).—Asbestos paper cannot be used in these analyses, since it does not absorb the blood efficiently. The best absorption paper is fairly thin, pure cotton-cellulose paper, which has been boiled with 10% aqueous acetic acid for 1 hr. and washed with water. G. A. C. Gough.

Determination of the total bases of the serum and other liquids by electrodialysis, and other applications of the method. R. Wernicke (Rev. inst. bacteriol., 1926, **4**, 7—13; Chem. Zentr., 1927, ii, 613).—A three-cell apparatus with two permanganate membranes was employed; the *P.D.* of 260 volts available between the platinum electrodes was regulated to give a current density of 0·04 amp./cm.^{2} With this apparatus cations were completely removed as hydroxides from solutions of their salts. The precipitation of proteins is also complete, and the method can be applied to anions containing oxygen. A. A. Eldridge.

Rapid determination of organic iodine in body fluids. P. Kuhn and A. Loeser (Arch. exp. Path. Pharm., 1928, **131**, 262—267).—A measured quantity of the organic material is heated in an iron crucible with sodium carbonate [(?) hydroxide] 1 part and potassium nitrate 2 parts. The mass after cooling is extracted with hot water, filtered, and the filtrate is carefully acidified. The iodine thus set free is extracted with chloroform, solid sodium hydrogen carbonate is added with vigorous shaking until the reaction is alkaline to litmus, and the iodine is then titrated with sodium thiosulphate. W. O. Kermack.

Determination of carbamide as dixanthylcarbamide. A. Boivin (Bull. Soc. Chim. biol., 1928, **10**, 684—698).—Carbamide, isolated from biological fluids as the dixanthyl derivative (A., 1927, 1067), may be determined by carbon analysis by the method of Nicloux (*ibid.*, 436). Silver chromate, originally employed in the analysis, is omitted, since its use leads to the formation of carbon monoxide. G. A. C. Gough.

Extraction of liquids. E. P. Widmark (Bull. Soc. Chim. biol., 1928, **10**, 669—674).—A new extraction funnel, consisting of two ordinary funnels joined some distance above the taps by a short wide glass tube, is described. Quantitative experiments show the advantages of this device, which is claimed to avoid the formation of emulsions in the extraction of fluids such as blood. G. A. C. Gough.

Ultrafiltration. A. Augsberger (Biochem. Z., 1928, **196**, 276—288).—The technique and theory of ultrafiltration of biological fluids are investigated and a method of preparing the membrane and of avoiding membrane and evaporation errors is given. The formation of a filtrate of constant composition is demonstrated with mixtures of gelatin or serum with sodium chloride. For gelatin and serum solutions of changing colloid content, a filtrate–time law is given according to which the filtration velocity is inversely proportional to the amount of filtrate. P. W. Clutterbuck.